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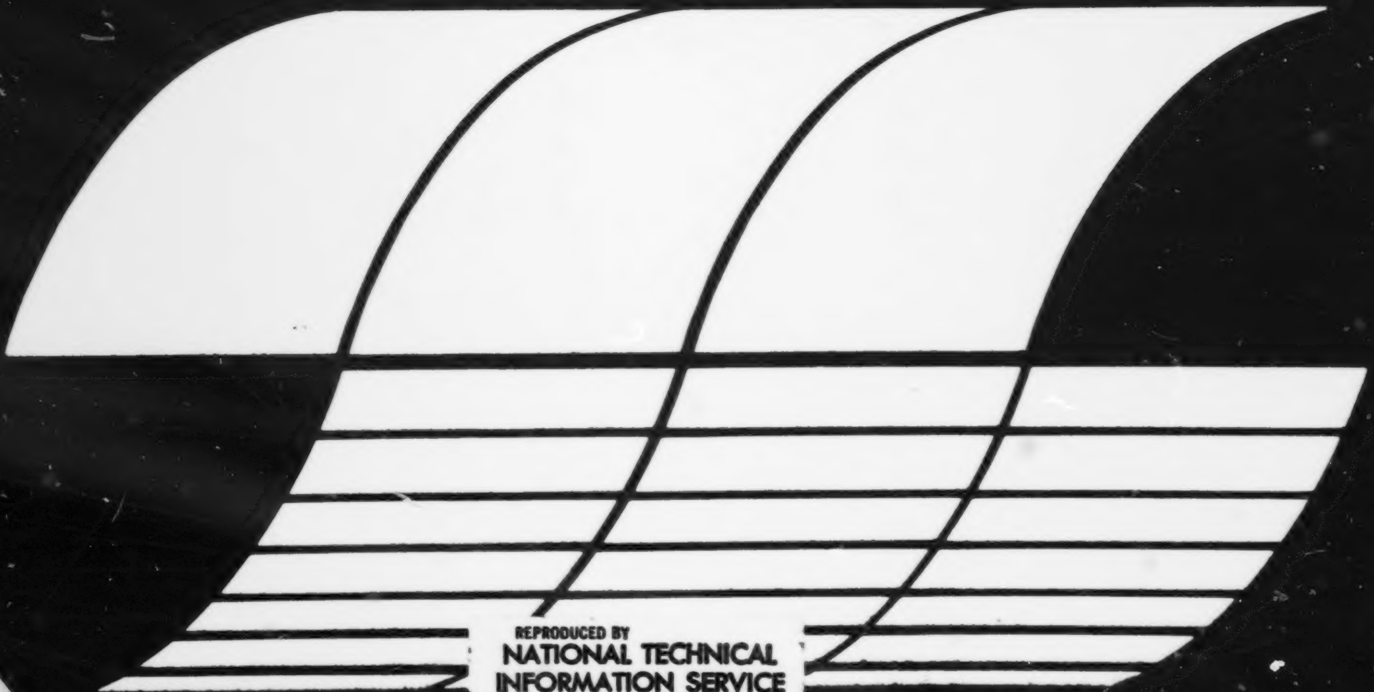

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a. DESCRIPTORS			b. IDENTIFIERS/OPEN ENDED TERMS			c. COSATI Field/Group		
Ecology	Hydrology, Limnology	Energy Conversion	Control Technology	Processes & Effects	Fuel	6F	8A	8F
Environments	Biochemistry	Physical Chemistry	Energy Conversion	Transport Processes	Coal			
Earth Atmosphere	Earth Hydrosphere	Materials Handling	Fuel Cleaning	Ecological Effects	Oil/Gas	8H	10A	10B
Environmental Engineering	Combustion	Inorganic Chemistry	Flue Gas Cleaning	[illegible]	Oil Shale			
Geography	Refining	Organic Chemistry	Direct Combustion	Health Effects	Nuclear	7B	7C	13B
		Chemical Engineering	Synthetic Fuels	Integrated Assessment	Geothermal			
			Nuclear	Energy Cycle	Solar			
			Thermal	Extraction	Waste as Fuel			
			Improved Efficiency	Processing	Hydroelectric			
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APPLICATION OF GERMANIUM DETECTORS TO ENVIRONMENTAL MONITORING

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SECTION 1

INTRODUCTION

The emphasis on monitoring the environment for radiological impact is growing with the increased use of nuclear power and the still prevalent concern over the effects of low-level radiation. One of the most economical and wide-ranging analytical tools for environmental monitoring is gamma-ray spectroscopy. However, obtaining accurate and reliable quantitative information from gamma-ray analysis requires a sophisticated and knowledgeable approach. This report examines the problems involved in applying germanium detectors to the analysis of environmental samples. All aspects of germanium spectroscopy are surveyed, with emphasis on equipment, installation of a system, quality control, energy and efficiency calibration, spectral analysis, analytical sensitivities, and cost considerations. We have tried to identify all significant literature in these areas, to evaluate different approaches, and to provide additional information on points often absent from the literature. Because the audience of the report is expected to have a good knowledge of gamma-ray spectroscopy and radiochemistry, no section has been included on basic aspects of these topics; however, references 1 through 11 can be consulted for assistance.

SECTION 2

CONCLUSIONS

Germanium detectors can be used to achieve analytical sensitivities of less than 10 pCi/L (for water) for most radionuclides. Depending on counting time and sample size, these sensitivities can be reached at a confidence level of 95 percent. However, a rough cost comparison with sodium iodide [NaI(Tℓ)] detectors indicates that the use of germanium detectors may not always be the more economical method of performing gamma-ray spectroscopy when factors such as initial capital outlay and volume of work are considered.

To be effective, germanium-based gamma-ray spectroscopy must use a method for spectral analysis that is accurate and reproducible, even with small changes in experimental conditions. Also, the corrections that affect each individual line of the calibration spectrum must be considered when efficiency calibrations are performed.

SECTION 3

RECOMMENDATIONS

Germanium detectors should be used to analyze environmental samples that may contain a complex mixture of radionuclides or unknown components because the resolution offered by germanium detectors is unexcelled in these applications. The analyst must be aware of pitfalls that may exist if undocumented software is used to analyze spectral data from germanium detectors. Programs such as GAMANAL, SAMPO, and HYPERMET are suggested as reliable tools, but newer techniques are available which may account more satisfactorily for the frequently encountered problem of poor counting statistics (see Section 5).

More effort should be given to establishing criteria for the evaluation of results produced by computer-analyzed spectra. Information on both fit and analysis of residuals is not commonly available to the analyst.

SECTION 4

GAMMA-RAY SPECTROSCOPY USING GERMANIUM DETECTORS

4.1 TERMINOLOGY

full energy peak (FEP): That region of a gamma-ray spectrum that is due to the complete energy transfer of a photon within the detector and the complete collection of the transferred energy within the detector. Full energy peak is also called total absorption peak or photopeak.

absolute full-energy peak efficiency: The fraction of emitted gamma-rays that are detected and recorded in the FEP of the pulse height distribution.[12]

absolute gamma-ray emission rate: The number of gamma rays of specific energy emitted per unit time from a radioactive source.

analog-to-digital converter (ADC): An electronic device used to convert a pulse amplitude into a digital form. This conversion is generally accomplished by converting a pulse of given amplitude into a number of equal time intervals by means of a clock pulse generator.[8]

blank sample: A sample that contains either no radioactive material or only low levels of radioactive material; such a sample is generally used to determine the background count rate for a radiation detector.

branching fraction: The probability of emission of a specific gamma ray per nuclear decay.

correlated photon summing: The simultaneous detection of two or more photons originating from a single nuclear disintegration.[13]

counts per second: A measure of the count rate for a radiation detector system for a given sample.

convolution: A mathematical transformation of data into a desired form. For gamma-ray spectral data this is accomplished by replacing the original data with data derived by multiplying the contents of selected channels by a series of convolution integers, integrating, and dividing the sum by a normalizing factor. The convolution and normalizing factors chosen determine the type of data transformation performed.[14]

direct current (DC) level: The reference input or output voltage for unipolar pulses on a DC coupled instrument. For germanium spectroscopy systems, the DC level of an output signal from a linear amplifier must be matched to the input requirements for DC level of an ADC for proper processing of pulse signals.

full width at half maximum (FWHM): The full width of a distribution measured at half the maximum ordinate. For a normal distribution, FWHM is equal to $2(2\ \ell n\ 2)^{\frac{1}{2}}$ times the standard deviation σ.[15]

full width at tenth maximum (FWTM): Same as FWHM, except that measurement is made at one-tenth, rather than one-half, the maximum ordinate.[15]

germanium detector: A semiconductor device that uses the production and motion of excess free charge carriers produced by absorption of radiation to detect and measure incident X and gamma radiation.[16]

Germanium detectors are of two general varieties: high-purity and lithium-drifted. A high-purity germanium (HPGe) detector is fabricated from hyperpure germanium crystals and contains an equal number of free acceptor sites and free charge carriers throughout its volume. Lithium-drifted germanium [Ge(Li)] detectors are fabricated by compensating ρ-type germanium with lithium ions, which are moved through a germanium crystal under an applied electric field in such a way as to compensate the charge of impurities bound to acceptor sites.[16] All germanium detectors are operated at liquid nitrogen temperatures, although HPGe detectors may be allowed to cycle to room temperature when no bias is applied. The response of a germanium detector is linearly proportional to incident photon energy.

germanium spectroscopy system: A gamma-ray spectroscopy system composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, a multichannel analyzer (MCA), a high-voltage power supply, and a lead or steel shield.

lower limit of detection (LLD): The smallest amount of sample activity, when a given measurement process (i.e., detector and chemical procedure) is used, that will yield a net count for which there is confidence at a predetermined level that activity is present.[17]

multichannel analyzer (MCA): A computer-like device used to store and retrieve digital information on pulse amplitude and frequency distribution. Generally, an array of magnetic or solid-state memories are used for data storage and manipulation.

peak-to-Compton ratio: Ratio of the maximum number of counts in a photopeak to the average height of the Compton continuum. The energy of the FEP and the radionuclide used must be stated.[15]

pole-zero cancellation: Compensation of pulse shape for the undershooting of the DC level (baseline) of the amplifier due to preamplifier fall time constant. Pole-zero cancellation is generally adjustable on amplifiers used for germanium spectroscopy and is set to minimize undershoot or overshoot of the pulse baseline.

random summing: The simultaneous detection of two or more photons originating from the disintegration of more than one atom.[13]

relative efficiency (in percent): The absolute FEP efficiency for the 1332.5-keV gamma ray emitted from a ^{60}Co source located 25 cm from the face of the germanium detector, relative to the corresponding efficiency of a 76- by 76-mm NaI(Tℓ) detector.

sensitivity: The minimum difference between two sample activities that can be statistically distinguished from each other at a determined confidence level.

sodium iodide [NaI(Tℓ)] detector: A radiation detector using a crystal of thallium-activated sodium iodide [NaI(Tℓ)], which scintillates when it interacts with X and gamma radiations. A generally linear relationship exists between light output of an NaI(Tℓ) crystal and incident gamma-ray energy. By using sensitive photocathode and photomutiplier units in conjunction with an NaI(Tℓ) crystal, an X- and gamma-radiation detector may be constructed. Typical spectral resolution for ^{137}Cs (661.6 keV) using a 10- by 10-cm NaI(Tℓ) spectrometry system is about 55 keV.

NaI(Tℓ) spectroscopy system: A gamma-ray spectroscopy system composed of an NaI(Tℓ) detector, an amplifier, an ADC, an MCA, a high-voltage power supply, and a lead or steel shield.

Type I error: The error committed in stating that the true activity is greater than zero when, in fact, it is zero.[18]

Type II error: The error committed in stating that the true activity is zero when, in fact, it is greater than zero.[18]

4.2 EQUIPMENT AND INITIAL SETUP OF THE SYSTEM

4.2.1 Equipment

Most basic gamma-ray spectroscopy systems using germanium detectors are composed of a germanium detector (with its cryostat, dewar, and preamplifier), an amplifier, a high-voltage power supply, a steel or lead shield, and an MCA with an ADC and data readout device. Other electronics can be added to the system, such as a liquid nitrogen monitor, a gain stabilizer, or a pulse pile-up rejector with live-time corrector. This report does not describe Compton suppression systems or any other type of coincidence system.

Liquid nitrogen monitors activate visual or audible alarms when the liquid nitrogen drops below a predetermined level. Because loss of liquid nitrogen may damage the detector and preamplifier [actually the field-effect transistor (FET)], a liquid nitrogen monitor may be valuable in certain laboratories. However, if a large-volume (30-L or larger) dewar is used and filled weekly, a liquid nitrogen monitor would not be needed.

Gain stabilization equipment should not be needed for most germanium systems because modern, high-performance electronic systems are generally stable (with a typical gain drift of only 0.03 percent per day). However, if a system is used to count samples for several days or weeks, gain stabilization may be needed to compensate for long-term gain variation.

A pulse pile-up rejector with a live-time corrector is used for samples with high count rates (e.g., greater than 5000 total counts per second). Typical environmental samples have low count rates, and pulse pile-up rejectors are not needed.

4.2.1.1 Germanium Detector

One principal component of the spectroscopy system is the germanium detector. Two basic types of detectors exist: the lithium-drifted germanium [Ge(Li)] detector and the high-purity germanium (HPGe) detector (often called an intrinsic germanium detector). Both detectors can be obtained commercially with high resolution and high efficiency. The HPGe has the advantage of being able to be warmed to room temperature, after removal of the detector bias, without damage to the detector.* The Ge(Li) detector would be seriously damaged if it were allowed to warm to room temperature under any circumstance. The HPGe detectors are now considerably more expensive than Ge(Li) detectors; however, they may begin to drop in price as they come into more common use.

High-efficiency (>15%) HPGe and Ge(Li) detectors can be fabricated in a true coaxial geometry or in a closed-end coaxial geometry. The closed-end coaxial detector is often preferred for counting environmental samples because it presents a more uniform, efficient cross section of active detector volume to samples that are counted a short distance from the detector.

Placement of the detector close to the cryostat endcap window is desirable because it is often necessary to place samples as close to the detector as possible. Typically, one can specify that the detector be placed within 5 mm of the cryostat endcap window and that the detector be mounted with azimuthal symmetry around the axis of the crystal. The symmetry is important when using a geometry such as a Marinelli beaker, which is one of the predominant environmental geometries now in use.

To ensure that a detector will have a good efficiency for samples counted at close geometries, the ratio of the detector diameter to the detector length should be as large as practical, typically greater than one.

The efficiency, resolution, and peak-to-Compton ratio basically determine the performance and cost of germanium detectors. Efficiency is a measure of the ability of the detector to detect a given level of activity. Resolution is a measure of the ability of a detector to differentiate between closely spaced lines. The larger the peak-to-Compton ratio, the better the detector can distinguish a low-energy FEP in the Compton ratio are generally specified in accordance with the Institute of Electrical and Electronics Engineers (IEEE) standard test procedures for germanium gamma-ray detectors.[15]

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*The detector and preamplifier will be damaged if the HPGe detector is allowed to warm up with the high voltage applied.

The relative efficiency in percent of the detector usually is specified for the 1332.5-keV gamma ray emitted from ^{60}Co at a source-to-detector distance of 25 cm relative to the corresponding efficiency of a 76- by 76-mm NaI(Tℓ) detector. The absolute FEP efficiency[19] for a 76- by 76-mm NaI(Tℓ) detector is 1.2×10^{-3}. Germanium detectors with 10 to 15 percent efficiencies are typically used for environmental analyses.

The energy resolution of a detector is expressed in terms of the full peak width in energy at one-half or one-tenth the maximum peak height (FWHM and FWTM). The FWHM is usually specified for the 122.1-keV gamma ray of ^{57}Co and the 1332.5-keV gamma ray of ^{60}Co. The FWTM is usually specified for the 1332.5-keV gamma ray. Typical ranges of values for the FWHM are 0.7 to 1.1 keV at 122.1 keV and 1.7 to 2.1 keV at 1332.5 keV. The FWTM at 1332.5 keV is typically a little less than twice the FWHM at the same energy. All resolution measurements are made after the background has been subtracted. The portion of the peak above the half-maximum should contain at least four channels, preferably more, so that the resolution can be measured accurately. Interpolation between channels is necessary to find the exact location of the half-maximum on each side of the peak centroid. The fewer channels in the peak, the less accurate the interpolation and thus the less accurate the value of the FWHM determined.

The peak-to-Compton ratio at 1332.5 keV is the ratio of the full peak height to the average height of the corresponding Compton plateau in the region below the edge (1040 to 1096 keV).[15] The peak-to-Compton ratio increases as the efficiency and resolution increase. Typical state-of-the-art peak-to-Compton ratios can be obtained from the vendors on request (usually from a list of specifications for detectors that have been recently delivered).

The cryostat, preamplifier, and dewar are generally supplied with the detector. Vertical cryostats with endcaps 20 to 25 cm long are generally preferred for environmental applications because Marinelli beakers, petri dishes, and other types of sources can be easily placed on the endcap. Longer endcaps may be necessary to ensure that the detector will fit into its shield.

Because the preamplifier and detector are generally integrated assemblies, specifying a given resolution will ensure that the preamplifier and detector are properly matched.

Many manufacturers offer a variety of dewars. A 30-L dewar is generally sufficient because it will hold more than a 20-day supply of liquid nitrogen. Even though the dewar has a long holding time, it should be filled every week as a precaution against accidental warm-up of the detector. Care should be taken to prevent blockage of the filling tubes with ice, which might result in the dewar appearing full when it is not.

Table 1 lists some nominal specifications for detector and shield. These detectors and shields were used to acquire data for parts of this report.

4.2.1.2 Amplifier

For routine sample analysis a spectroscopy* linear amplifier is generally used. Certain specifications are adequate for most needs and can be met by most suppliers of nuclear instruments: (1) temperature stability--gain <0.01 percent per degree Centigrade from 0 to 50°C and DC level <±5 μV/°C from 0 to 50°C; (2) integral nonlinearity--<±0.05 percent of full rated range of the output; and (3) noise--<5 μV referred to input with a gain of 3000 and a 2-μs time constant. The amplifier should be equipped with a baseline restorer. The amplifier should be supplied with a connector on the rear panel, which is properly wired to supply the appropriate power to the detector preamplifier. Additional specifications may be needed for particular applications. Consult IEEE Standard 301-1969[20] for amplifier test procedures.

4.2.1.3 Bias Supply for Detector

The bias supply for the detector should have a voltage range to accommodate the detector; typically, a range of either 0 to 3 or 0 to 5 kV is adequate for most detectors. The voltage should be continuously adjustable over the full operating range with a front-panel meter for monitoring the output voltage. A bias supply with a temperature stability of about 0.02 percent per degree centigrade and noise and ripple of less than 10 mV peak-to-peak from 2 Hz to 5 MHz should be adequate for most applications. One should ensure compatibility of the connector on the supply with the cable and connector on the preamplifier.

4.2.1.4 Shield

Shields of low-activity steel or lead are generally used. Lead has a much higher gamma absorption coefficient than steel in the photoelectric and pair production range, but low-activity steel is easier to locate than low-activity lead.[21]

Backscatter within the shield decreases as the atomic number of the shielding material increases. Thus, lead shields have a much lower backscatter component than do steel shields.[22] The backscatter component also decreases as the internal dimensions of the shield increase.[22] Typical internal dimensions are 41 by 41 by 41 cm to 61 by 61 by 61 cm. Most lead shields have a 0.08-cm cadmium liner to degrade lead X rays and

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*Several vendors designate amplifiers that are to be used with germanium detectors as spectroscopy amplifiers. However, this is not a generally accepted grade designation for an amplifier and should not be solely used in specifying an amplifier.

TABLE 1. NOMINAL DETECTOR AND SHIELD SPECIFICATIONS

Specification	Detector 1	Detector 2	Detector 3
	Detector		
Type	True coaxial	Closed-end coaxial	Closed-end coaxial
Resolution-FWHM, keV			
122.1 keV	1.41	1.02	0.731
1332.5 keV	2.23	1.99	1.99
Efficiency[a] at 1332.5 keV, %	8.7	14.3	16.0
Diameter, mm	42	50.0	47.5
Length, mm	36	44.5	41.0
Diffusion depth, mm	21.7	15.5	17.75
Active volume, cm^3	48	70	80
p-Core diameter, mm	8.5	-	-
	Shield		
Shield thickness, cm	10	15	15
Material	Lead with graded absorber	Steel with graded absorber	Steel with graded absorber
Inside dimensions (L x W x H), cm	36 x 36 x 81	41 x 41 x 41	41 x 41 x 41

[a] Relative to the corresponding efficiency of a 76- by 76-mm NaI(Tℓ) detector with source placed 25 cm from the detector face.

a 0.04-cm copper liner to degrade cadmium X rays.[22] In addition to the cadmium and copper liners, steel shields may have a 0.6- to 1.2-cm lead liner to remove some of the low-energy background.

All shields should be designed to prevent any direct paths for radiation leakage. Provisions should be made for easy insertion of the germanium detector into the shield while providing adequate space for the preamplifier and its cables. Shock-absorbing material should be placed around the closure opening to prevent any mechanical shock to the detector as the shield is opened or closed.

Typically, steel shields are 15 cm thick and lead shields are 10 cm thick. The loading capacity of the floor of the counting room should be considered when shields are purchased. Provisions for installing the shields should also be made at the time of purchase.

4.2.1.5 Multichannel Analyzer System (MCA)

Although a full discussion of MCA systems is beyond the scope of this report, limited information is given. The MCA system is composed of one or more ADCs, the MCA, and assorted input/output (I/O) peripherals.

The ADC is generally purchased with the MCA. If both are not purchased from the same vendor, care should be taken to ensure compatibility of the MCA and ADC.

An ADC for germanium spectroscopy of environmental samples should meet certain specifications: (1) conversion gain--at least 8192, 4096, 2048, 1024, and 512 channels; (2) internal clock frequency--≥50 MHz, crystal controlled; (3) integral nonlinearity--≤0.05 percent over 99 percent of the full range; (4) differential linearity--≤1.0 percent deviation from the mean channel width over 99 percent of the full scale; and (5) stability--time, better than ±0.01 percent per day at stable ambient temperature and line voltage; and temperature, better than ±0.01 percent per degree Centigrade from 15 to 40°C.

The output pulse characteristics of the amplifier and the input requirements of the ADC should be compatible. This is no problem for most combinations of amplifiers and ADCs. The ADC should have a live-time corrector and a dead-time meter.

Two basic types of MCAs are available: nonprogrammable MCAs (NP-MCA) and fully programmable MCAs (P-MCA). An NP-MCA has been termed a hard-wired MCA, but this classification does not necessarily apply because many newer NP-MCA units are built around a microprocessor.

The decision of which type of analyzer and what options to purchase is very complex. An NP-MCA is relatively easy to use for collecting data, is less expensive, and is generally more reliable. A P-MCA is capable of executing data reduction and other programs and is generally more flexible. A P-MCA can accept multiple ADC inputs, whereas most NP-MCA units are only able to accept one ADC input. When several detector systems are used, a single P-MCA system can be used for all the detector systems, whereas several NP-MCA systems would be required. Also, the P-MCA can be used to analyze spectra. A total analysis and reduction system using a P-MCA with several detector systems to collect and analyze spectra may be less expensive than one using multiple NP-MCA systems.

The choice of I/O peripherals for a system depends on the requirements of the individual laboratory. Most laboratories will need some hardware for storing spectra. Magnetic tape and disk are frequently used. Also, some type of fast printer and a plotter are usually desirable.

4.2.1.6 Summary

Each component of the system should be specified and chosen with care. The current state-of-the-art can be determined by studying several vendors' catalogs, consulting representatives of the vendors, and discussing appropriate topics with experienced spectroscopists.

In general, the detector, amplifier, and bias supply should be bought as a system from the same vendor. The MCA, ADC(s), and I/O peripherals usually are bought as a system from the same vendor. Buying a complete system from a single vendor may prevent noncompatibility of individual components and may eliminate the problem of dealing with many vendors for equipment maintenance. One should request three copies of all instrument manuals--one to give to the instrument shop, one to keep with the instrument, and one to file. Also, all connectors, cables, and nuclear-instrument-module (NIM) bins should be included in the order as needed.

4.2.2 Initial Setup

If the detector and MCA systems are purchased from one vendor, most vendors will install and demonstrate the system. Although many laboratories have trained spectroscopists capable of installing the system, it is a good policy to allow the vendor representatives to install the system because they can confirm any damage or nonconformance to specifications.

If a laboratory finds it necessary to set up the system, all manuals supplied by the manufacturer should be thoroughly reviewed. Manufacturers' instructions for setting up and testing the system should be followed. Any questions about setting up the equipment should be directed to factory representatives.

4.3 QUALITY CONTROL

After the system is set up, one must ensure that the system always performs reliably. Reliable operation can be assured by using quality control procedures designed to detect any system malfunction at the earliest possible moment. American National Standards Institute (ANSI)

Guide N717[13] suggests tests for (1) energy calibration, (2) count rate reproducibility, (3) system resolution, and (4) efficiency calibration. Also, Zeigler and Hunt[9] suggest (1) background stability, (2) MCA time base, and (3) MCA live time checks. Tests are also recommended for (1) detector leakage current, (2) detector peak-to-Compton ratio, (3) system linearity, (4) amplifier adjustment (pole-zero and DC level), and (5) system noise.

The detector leakage current test is discussed in Appendix A. Typical procedures for other quality control tests are given in Appendix B. These procedures have been written to exclude references to specific equipment and instrument settings.

When using these quality control procedures, one must specifically identify (by model number and serial number) the equipment being tested and record the instrument settings on a form (similar to that in Figure 1), which is attached to the logbook for the specific system. When system components or instrument settings are changed, the date of the change is recorded on the form, and a new form is filled out and entered in the logbook.

Control charts are used to monitor statistically the reproducibility of the detector system over a period of time. Both background and efficiency are readily monitored by use of control charts. References 23 through 25 discuss the construction of control charts, and references 9, 17, and 26 discuss their application to nuclear counting instruments.

In addition to an instrument quality control program for ensuring stable instrument performance, an analytical quality control program should be developed to ensure that reproducible and accurate analytical results are obtained. The analytical quality control program should use replicate analyses, spiked samples, and collaborative sampling to monitor precision and accuracy. Kanipe[26] gives a detailed discussion of analytical quality control. Programs such as the EPA-Las Vegas cross-check program provide an excellent source for regular interlaboratory comparisons.

4.4 CALIBRATION

4.4.1 Energy Calibration

An accurate energy calibration for a germanium detector system is required for assignment of correct energies to the centroid of each FEP in an unknown spectrum. Procedures for identifying the radionuclides within a spectrum rely on methods for matching the energies of the principal gamma rays in the spectrum to the energies of gamma rays emitted by radionuclides that are likely components of a particular sample. This procedure can be accomplished by either manual inspection or computer analysis. Several criteria should be examined before a final identification is accepted (Section 5.1.4); these checks include determining that all intense gamma rays are present and that the intensity ratios are correct.

Procedure: ______________________________

Usage Date   Begin: ______   End: ______

Detector: ______________________________

Power Supply: ______________________________

Voltage: ______________   Polarity: ______________

Amplifier: ______________________________

Coarse Gain: ______________________________

Fine Gain: As specified in the system logbook daily entry page __________.

Input Polarity: ________   Shaping ________Microseconds

Polarity: ________   Range: ________   Restorer: ________

ADC: ______________________________

Conversion Gain: ______________________________

Group (or group selection, if so equipped): ________

Upper Level Discriminator (or ULD): ______________

Lower Level Discriminator (or LLD): ______________

Analog Zero (or zero or fine zero): ______________

Zero Suppression (if so equipped): ______________

Other Switches: ______________________________

Interconnections: ______________________________

____

MCA: ______________________________

Experiment: ______________   ADC: ______________

Channels: ______________   Preset Time: Live

Groups: ______________

I/O Assign:

Input: ______________   Subselect: ________

Output: ______________   Subselect: ________

Other: ______________________________

____

____

Figure 1. System check-out form.

The energy calibration of a germanium detector system is generally given by a mathematical function, the analytical form of which will depend on the linearity of the system. The energy calibration of an essentially linear system can be described satisfactorily by a straight line. The appropriate expression is determined from two calibration points by

$$G = (E_2 - E_1)/(C_2 - C_1) \tag{1}$$

and

$$F = E_1 - (G)(C_1) , \tag{2}$$

where

E_1 and E_2 = energies of calibration lines 1 and 2,

C_1 and C_2 = channels corresponding to the centroid of the FEPs of lines 1 and 2,

G = gain of the system, in energy units/channel,

F = offset of the system, in energy units.

The centroid channel, offset, and gain can then be used to calculate the exact energy of an FEP by the expression,

$$E = F + (G)(C). \tag{3}$$

The FEPs selected for calibration points should be separated in energy by as much as is practical. ANSI Guide N717[13] recommends that the energy separation of the calibration points be at least 50 percent of the spectral range of interest. A least-squares fit of several calibration points is required when highly accurate energy assignments are needed or when the system is nonlinear.[27,28] Peak positions and energies are usually fit to a polynomial equation of the general form,

$$E = \sum_{j=1}^{N} A_j (C)^{j-1} , \tag{4}$$

where

E = energy of the calibration line,

C = channel corresponding to the centroid of the FEP,

A_j terms = fit parameters.

Gleason[28] proposed a variation of this equation to describe certain types of nonlinearities often found in older ADCs:

$$E = A_1 + (A_2)(C) + A_3/C^2 . \tag{5}$$

All parameters are defined as for equation (4). In all the equations described above, the zero-order term, in channel number, specifies the zero-channel intercept. The first-order term, in channel number, specifies the system gain, and the additional terms describe the system nonlinearity. Table 2 lists energy calibration data obtained by using a National Bureau of Standards (NBS) mixed-radionuclide standard point source[29] and appropriate energy values taken from Heath.[30] A plot of the energy calibration data using the 88.036-keV ^{109}Cd line and the 1332.483-keV ^{60}Co line as calibration points is shown in Figure 2. Figure 3 is a plot of the system nonlinearity, measured as the deviation of the actual data from the linear, least-squares-fitted data. For routine environmental analyses, linear energy calibrations often can be used when systems exhibit only small nonlinearities, such as those shown in the example.

Complex energy calibration techniques, such as least-squares fits to second-, third-, or higher-order polynomials, may not be justified when the sample spectra contain many peaks that are not statistically well defined (i.e., that contain a small number of counts). The centroid of peaks with poor statistics cannot be defined with sufficient accuracy to derive accurate energy data from the peaks; therefore, no real benefit is gained from the complex calibration procedure. An energy calibration that is accurate to ±0.1 keV may not be necessary when peaks in the sample spectra cannot be located to better than ±1 or ±2 keV.

4.4.2 Efficiency Calibration

An accurate calibration of efficiency is necessary to quantify effectively any radionuclides present in a sample. Great care must be exercised in calibrating the efficiency because the accuracy of all quantitative results depends on this calibration. Before determining the efficiency, one should select, properly connect, and properly adjust the components (germanium detector, shield, amplifier, ADC, and MCA) of the system (Section 4.2). Certain settings and adjustments of the amplifier, for example, should be maintained until a new calibration is undertaken. Changes in amplifier time constants and baseline restoration settings may have slight, but direct, effects on counting efficiency. Adjustments in pole-zero cancellation and DC level can change the peak shape. Changes in peak shape affect the determination of the FEP count rate and thus produce changes in the efficiency.

One should consider several points before undertaking the actual determination of efficiency: (1) sample counting configuration, (2) calibration methods, (3) calibration sources, and (4) analytical efficiency expressions.

4.4.2.1 Sample Counting Configuration

For routine, reproducible sample analysis, counting containers must be selected on the basis of both the volume of sample available and the optimum counting configuration. In general, the optimum geometry would give the highest sensitivity (i.e., the lowest limit of detection). If the method used by the Health and Safety Laboratory (HASL) (Section 5.2) were adopted, the LLD would be given by

TABLE 2. ENERGY CALIBRATION DATA

Energy[a] (keV)	Location of peak centroid (channel)	Error[b] (keV)	
		Using two calibration points	Least-squares fit
88.036	176.05	0.000	0.151
122.060	244.16	0.030	0.172
136.471	272.97	0.024	0.163
165.854	331.74	0.141	0.157
279.190	558.17	-0.098	0.007
391.689	783.07	-0.149	-0.072
513.998	1027.45	-0.270	-0.222
661.63	1322.83	-0.215	-0.203
898.00	1795.59	-0.209	-0.255
1173.226	2346.22	-0.125	-0.238
1332.483	2664.99	0.000	-0.151
1836.075	3673.72	0.764	0.490
Gain		0.5000	0.4999
Offset		0.0126	0.1845

[a] The energy values are taken from a compilation by Heath.[30]

[b] The error is the difference between the calculated value and the measured value.

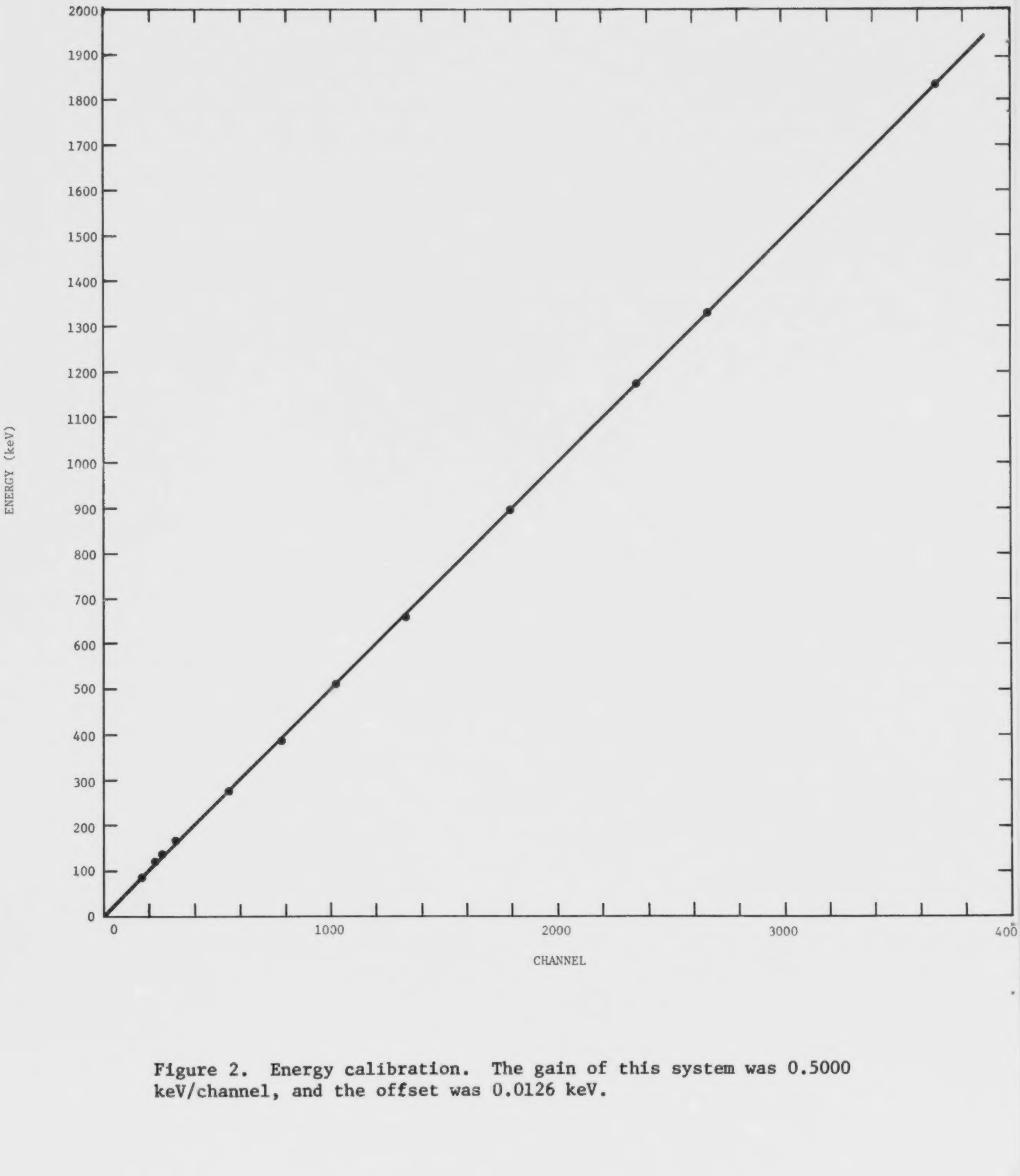

Figure 2. Energy calibration. The gain of this system was 0.5000 keV/channel, and the offset was 0.0126 keV.

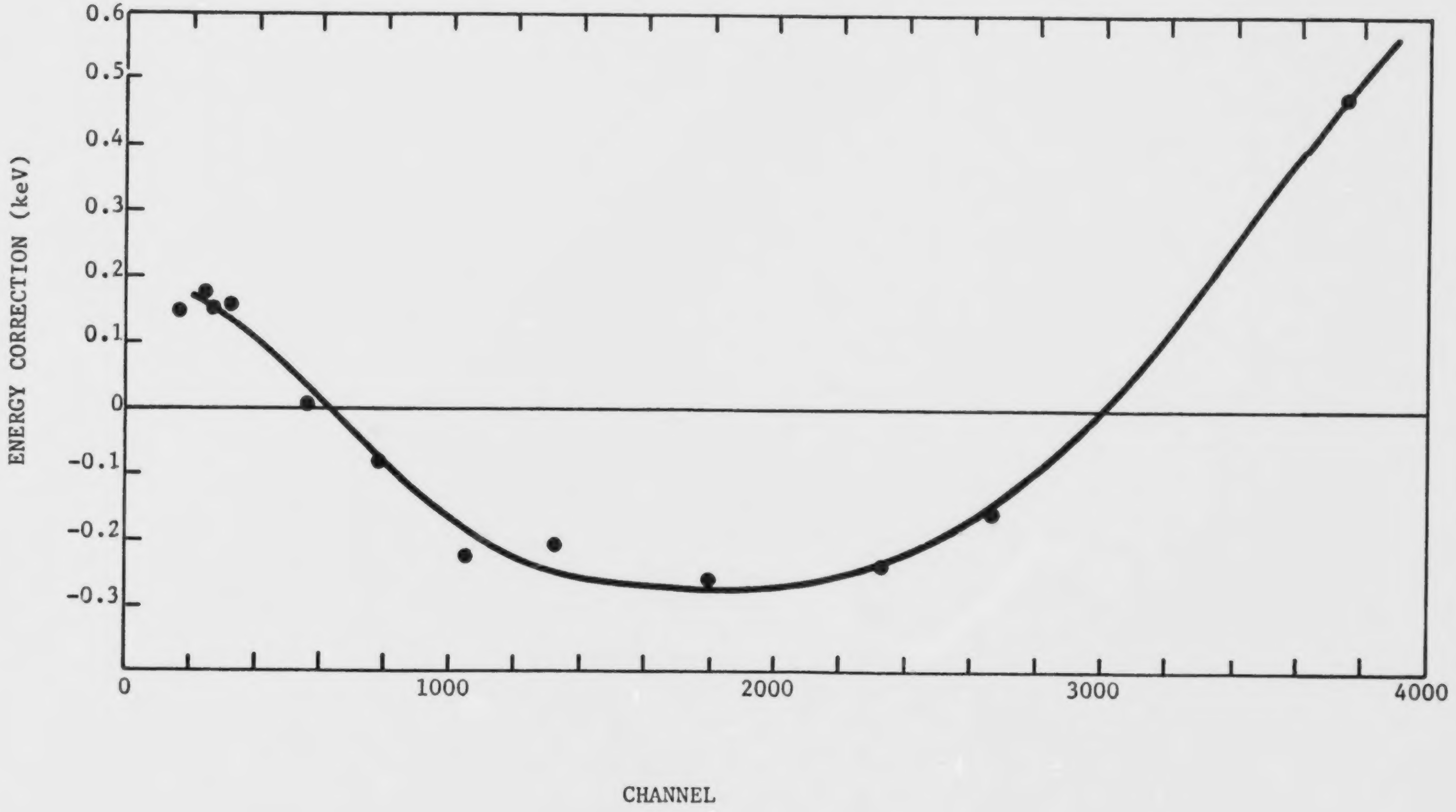

Figure 3. Nonlinearity of a typical system. A linear least-squares fit of the data used for Figure 2 yields a gain of 0.4999 keV/channel and an offset of 0.1845 keV.

$$\text{LLD} = 4.66\sqrt{S_b}/(\text{RVEfDA}\sqrt{t}) , \quad (6)$$

where

LLD = lower limit of detection,
S_b = background count rate in the region of interest,
R = chemical yield or recovery for all steps in the procedure,
V = sample volume or mass,
E = counting efficiency,
f = number of photons of a given energy per nuclear decay (i.e., the branching fraction),
D = radioactive decay fraction,
A = unit conversion factor,
t = length of the counting time interval.

The background count rate, counting efficiency, and sample volume or mass vary directly with the counting configuration selected. The other parameters are selected for a given sample or held constant for a particular analysis. In general, changes in sample configuration produce only small changes in the background rate and therefore produce even smaller changes in the sensitivity, which is proportional to the square root of the background rate. As the sample volume or mass increases, counting efficiency decreases, because in a physically larger sample, emitted gamma rays will subtend a smaller solid angle at the detector. Therefore, the product of the counting efficiency and sample size must be optimized within reasonable limits to achieve optimum sensitivity. For most practical applications, Marinelli beaker geometries provide optimum sensitivity. Table 3 compares several different counting configurations.

The TVA Radioanalytical Laboratory at Muscle Shoals counts soil, vegetation, and some liquid samples in 0.5-L Marinelli beakers,*[17] other liquid samples in 3.5-L Marinelli beakers,** and air filters and certain biological samples in 60- by 15-mm petri dishes. Other commonly used sample containers are listed by Zeigler and Hunt.[9]

All sample containers are centered on the detector endcap. Positioning of the sample containers must be reproducible because a small variation in sample geometry can cause a large variation in count rate when the source is close to the detector. Marinelli beakers may be

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*0.5-L Marinelli beakers are available from Control Molding Co., 84 Granite Avenue, Staten Island, NY, 10303.

**3.5-L Marinelli beakers are available from GA-MA and Associates, Inc., P.O. Box 480091, Miami, FL 33148.

TABLE 3. COMPARATIVE LLD VALUES[a] (pCi/L) FOR VARIOUS MARINELLI GEOMETRIES

Nuclide	Energy (keV)	LLD values by Marinelli geometry		
		0.5-L	1-L	3.5-L
^{144}Ce	133	127	94	54
^{137}Cs	662	19	14	4
^{88}Y	898	19	15	7
^{60}Co	1173	25	13	3
^{60}Co	1332	19	13	3
^{88}Y	1836	16	14	-

[a] LLDs are calculated by the method developed by Harley.[17] They are for a 900-min sample count using detector 1 (Section 4.2, Table 1).

allowed to touch on the cryostat endcap (with the sample weight resting on the shield) and centered by using a collar or spacer around the endcap. Any positioning method can be tested by repeated removal and replacement of the source, with each replacement being followed by a measurement of the count rate for a sufficient time to minimize statistical fluctuations. A consistent count rate will indicate that a reproducible counting geometry has been achieved.

4.4.2.2 Calibration Methods

Three primary methods of efficiency calibration are in use: (1) theoretical Monte-Carlo methods, (2) theoretical efficiency models with experimentally determined parameters, and (3) experimental determinations.

Theoretical calculations of efficiency detection by Monte-Carlo methods[31-35] have been limited to point or disc sources because calculations for more complex sample configurations are difficult, time-consuming, and relatively inaccurate. Also, because detectors come in many sizes and shapes, a calculation would be necessary for each geometry contemplated for use with each detector. Theoretical calculations of detection efficiency are further complicated by the different interactions that can occur under identical circumstances. For example, effects such as bremsstrahlung, annihilation, escape, backscatter, multiple internal scattering, pulse pile-up, statistical fluctuations in the pulse-height conversion, and inhomogeneity in the detector are difficult or impossible to account for properly in Monte-Carlo calculations.[11]

To use the Monte-Carlo technique effectively, a description of the physical geometry of the germanium detector must be available. The precise definition of the active volume of a germanium detector is difficult to determine because the boundaries of the active area are diffuse. Also, the precise location of the crystal within the cryostat must be determined by radiographic or gamma-scanning methods because the copper cold-finger will contract when cooled to the temperature of liquid nitrogen, thereby changing the location from that observed at room temperature. In addition to these difficulties, certain inherent systematic errors depend on the Monte-Carlo model chosen and on the approximations made for the energy loss of secondary electrons.[36] One should attempt to calculate and use theoretical detection efficiencies only after making a thorough search of the literature and considering the difficulties. Such theoretical calculations now appear too uncertain for routine use and too time-consuming for most laboratories to perform regularly.

The Lawrence Livermore Laboratory has developed a model that combines theoretical calculations with experimentally defined parameters to describe the overall efficiency of a germanium detector as a function of gamma-ray energy, source-to-detector distance, dimensions of the detector, extension of the source in area and volume, composition of the source, external absorbers, and the dead layer of the detector.[27,37] This model has been applied to point, disc, and cylindrical sources.

Measurement errors of 1 to 2 percent are typical for small-volume sources, regardless of energy or source-to-detector distance. Large-volume sources placed close to the detector are accurate to within 10 percent. The measurement errors were evaluated by comparing the values determined by the model with the known value of the standards. Because this model can handle only point, disc, and cylindrical geometries, its usefulness is quite limited. Effective use of the model also requires a sizable computer for data analysis and a staff with considerable knowledge of germanium detectors to make the necessary measurements. This model should be considered when calibration techniques are being reviewed, but the advantages and difficulties of implementation should be carefully evaluated.

The most common approach to calibration of germanium detectors is the experimental determination of FEP efficiency as a function of energy for each counting configuration. Practical calibration standards for each counting configuration must be prepared from appropriate, calibrated radionuclides. The composition of these standards should approximate as closely as possible, with respect to density and attenuation factors, the actual samples that are to be analyzed after calibration. Laichter et al.[38] prepared solid calibration standards using evaporated sea water and tabulated mass attenuation coefficients for representative solid environmental and biological media. One can use granulated salt to represent soil and vegetation samples. Finely shredded styrofoam is used to adjust the density of the solid standards to correspond to the density of the various environmental samples. Small volumes of radioactive solutions are thoroughly mixed with the salt and styrofoam. Food coloring is used to indicate the degree of mixing.

Water samples are easily prepared by using acidified water with appropriate concentrations of carrier solutions.

Experimental determination of the FEP efficiency as a function of energy for each counting configuration does not require the sophisticated computer codes or the measurement of detector characteristics (dead layers, dimensions of the active volume of the detector, position of the detector within the cryostat endcap, etc.) that are required for the first two methods. Also, the experimental method is not subject to the uncertainties associated with the theoretical or semitheoretical models chosen to calculate the detection efficiency. However, the experimental method is time-consuming because of the number of samples that must be prepared and counted, but the time required to prepare and count samples may be less than that required to set up the necessary computer programs and perform and verify the calculations suggested for the first two methods.

Techniques for handling and storing radioactive solutions are beyond the scope of this report, but several excellent reports are available.[26,39,44]

4.4.2.3 Calibration Sources

Appropriate gamma-emitting radionuclides must be selected for use as standards in calibration. Characteristically, calibrated solutions of these radionuclides should be readily available, in a pure form, and have an accurately measured, relatively long half-life (greater than 30 days).

Accurate, absolute gamma-ray emission rates must be available for calibration standards. These activities are reported in terms of nuclear disintegration rates (e.g., sec^{-1}, Curie), although standards for gamma-ray emission rates can be used directly to determine efficiency (Section 4.4.2.4). The best source of gamma-ray emission rates and other decay information is the Nuclear Data Sheets,[45] published monthly by Academic Press. The latest mass entry in Nuclear Data Sheets can be used with the volumes entitled Recent References to obtain the latest references to data on any radionuclide. A certificate of calibration, which conforms to the recommendations of the International Commission on Radiation Units and Measurements,[46] should accompany all standards. The information supplied must include activity, uncertainty, reference date, description of purity, method of measurement, chemical composition, volume or mass, and values for decay corrections such as half-life and branching fractions.

Radionuclides that are used to determine efficiency can be classified into two groups: (1) those radionuclides with only a few prominent gamma rays and (2) those radionuclides with many prominent gamma rays. The radionuclides listed in Table 4 belong to the first category and have been extensively used for efficiency calibrations.[47-49]

Several radionuclides can be used either singly or in combination to determine an efficiency curve for a germanium detector over an energy range of 10 to 2800 keV. The energy range of interest must be adequately covered by calibration points so that interpolations between calibration points are accurate. ANSI Guide N717[13] suggests points every 100 keV from 60 to 300 keV, every 200 keV from 300 to 1400 keV, and at least one between 1400 and 2000 keV. Such a spacing of calibration points will clearly define the region from 60 to about 300 keV if large variations in efficiency are prevalent.

Many radionuclides of the second category have been suggested, but the most frequently used sources are ^{56}Co, ^{75}Se, ^{110m}Ag, ^{133}Ba, ^{152g}Eu, ^{182}Ta, and ^{226}Ra and its short-lived daughters.[36,49-63] The approximate ranges of energies in which each radionuclide is useful are ^{56}Co--840 to 3500 keV; ^{75}Se--120 to 400 keV; ^{110m}Ag--650 to 1600 keV; ^{133}Ba--30 to 400 keV; ^{152g}Eu--40 to 1400 keV; ^{182}Ta--100 to 270 keV and 1000 to 1250 keV; and ^{226}Ra and its short-lived daughters--180 to 2400 keV. For source-to-detector distances of 10 cm or less, correlated photon-summing corrections should be made for radionuclides that emit gamma rays in cascade with the gamma ray of interest (Section 4.4.2.4). The complexity, magnitude, and uncertainty of these summing corrections lead most laboratories to use several radionuclides with few prominent gamma rays. Even some commonly used radionuclides (^{134}Cs, ^{94}Nb, ^{46}Sc, ^{88}Y,

TABLE 4. STANDARDIZATION SOURCES

Nuclide	Half-life[a]	Radiation	Photon energy[a] (keV)	Number of photons emitted per decay[a]
^{22}Na	2.60y	γ ray	1274.5	0.9995
^{24}Na	15.0h	γ ray	1368.5	1.000
		γ ray	2754.0	0.9985
^{46}Sc	83.7d	γ ray	889.2	0.9998
		γ ray	1120.5	0.9999
^{51}Cr	27.8d[b]	γ ray	320.1[c]	0.098[c]
^{54}Mn	312.5d	γ ray	834.8	0.9998
^{57}Co	272.0d[d]	γ ray	14.4	0.096
			122.1	0.856
^{60}Co	5.27y	γ ray	1173.2	0.9988
		γ ray	1332.5	0.9998
^{85}Sr	64.8d	K_α x-rays	13.4	0.507
		γ ray	514.0	0.9928
^{88}Y	106.6d	K_α x-rays	14.2	0.525
		γ ray	898.0[d]	0.914[d]
		γ ray	1836.1	0.994
^{94}Nb	2.0 x 10^4y[b]	γ ray	871.1	1.000[c]
^{95}Nb	35.15d	γ ray	765.8	0.9980
^{109}Cd	450.0d[b]	γ ray	88.0[c]	0.0372[c]
^{113}Sn	115.2d	K_α x-rays	24.1	0.795
		γ ray	391.7[c]	0.649[c]
^{131}I	8.02d	γ ray	364.5	0.824

TABLE 4 (continued)

Nuclide	Half-life[a]	Radiation	Photon energy[a] (keV)	Number of photons emitted per decay[a]
^{134}Cs	2.06y	γ ray	604.6	0.975
^{137}Cs	30.0y	K_α x-rays	31.8/32.2	0.0564
		γ ray	661.6	0.853
^{139}Ce	137.6d	K_α x-rays	33.0/33.4	0.641
		γ ray	165.8	0.800
^{141}Ce	32.5d	K_α x-rays	35.6/36.0	0.126
			145.5	0.800
^{140}La	40.27h	γ ray	1596.6	0.956
^{198}Au	2.696d	γ ray	411.8	0.9553
^{203}Hg	46.6d	K_α x-rays	70.8/72.9	0.101
		γ ray	279.2	0.813
^{207}Bi	30.0y[b]	γ ray	1063.6[c]	0.753[c]
^{241}Am	433.0y[d]	L_α x-rays	13.9[d]	0.135[d]
		L_β x-rays	17.8[d]	0.210[d]
		L_γ x-rays	20.8[d]	0.050[d]
		γ ray	26.4[d]	0.025[d]
		γ ray	59.5[d]	0.359[d]

[a] All data, unless otherwise noted, is from Debertin et al.[48]

[b] Data from Heath.[30]

[c] Data from Hirshfeld et al.[47]

[d] Data from Hansen et al.[49]

^{60}Co, ^{24}Na, and ^{140}La) require summing corrections. Typical magnitudes of correlated photon-summing corrections for radionuclides from the first and second categories are given in Section 4.4.2.4.

The NBS issues mixed-radionuclide, emission-rate standards in point-source form and in solutions of different concentrations.*[29,64] These standards provide eleven principal gamma rays covering the energy range of 90 to 1800 keV in reasonably well spaced intervals. Figure 4 shows a typical gamma-ray spectrum observed from part of one solution. The standards were originally developed for calibrating germanium detectors for environmental analyses.[65] This annual mixed-nuclide standard is issued each September. The solutions are easy to use and offer the added advantage of traceability to NBS. Only two radionuclides, ^{60}Co and ^{88}Y, must be corrected for summing (see Section 4.4.2.4, Table 5). An excellent description of these standard solutions and potential problems associated with their use has been given by Coursey.[29] Other suppliers of calibrated radioactive materials are listed in the International Directory of Certified Radioactive Materials.[65]

4.4.2.4 Efficiency Determination

After an experimental method for determining efficiency has been selected, count-rate data must be acquired by using the appropriate calibration sources. Before actual standardization is begun, the spectroscopy system should be thoroughly tested to ensure electronic stability (Sections 4.2 and 4.3). The calibration sources then must be carefully prepared with a total activity low enough that random summing is negligible. Random summing is a function of the shaping times of the amplifier, because the shaping times determine the pulse width, which in turn determines the probability of random summing. Count rates of 5000 total counts per second or less can be used with shaping times of 1 μs or less[13] without appreciable summing, whereas 2500 and 1250 total counts per second or less can be used with amplifier shaping times of 2 or 4 μs or less, respectively.

The standard source should be carefully positioned in the detector shield, and spectra should be acquired which contain a statistically sufficient number of counts in each FEP of interest. ANSI Guide N717[13] suggests a minimum of 20,000 net counts in each FEP. If one assumes that the background counts are negligible, compared with the FEP counts, 20,000 counts will give a 0.7 percent counting uncertainty at a 68 percent (1σ) confidence level. Once the calibration spectra have been obtained, the net count rate must be determined for each FEP of interest. Any method that yields consistent results may be used to determine net count rate, but the method selected should yield the highest efficiency while minimizing the background contribution to the FEP region (Section 5.1.3).

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*Amersham/Searle Co., 2636 S. Clearbrook Drive, Arlington Heights, Illinois 60005, has developed a mixed radionuclide emission rate standard that is traceable to NBS and will be available quarterly. This standard has the identical composition of the NBS standard.

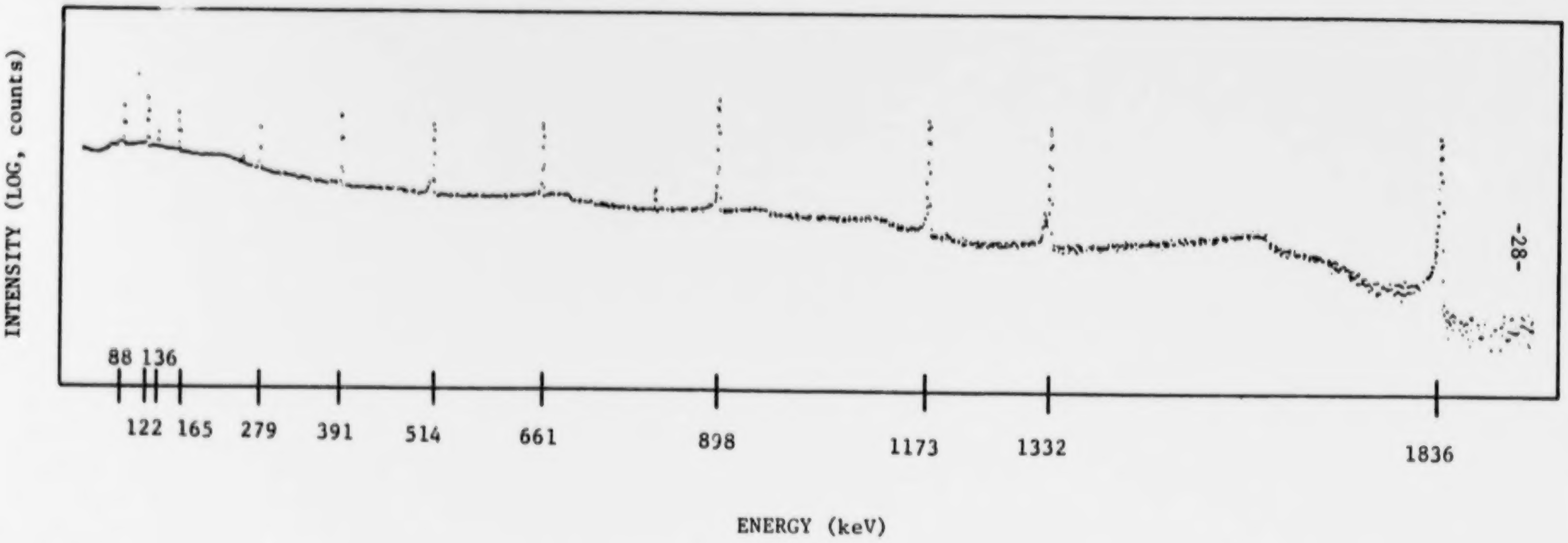

Figure 4. Typical gamma-ray spectrum detector. Observed from an NBS mixed-radionuclide gamma-ray standard.

When source-to-detector distance is 10 cm or less, correlated photon-summing corrections should be applied to the count rates of all gamma rays being used in the calculations that are emitted in cascade with other gamma rays. The correction factor for summing, S, is given by

$$S = 1/\prod_{i}^{n} (1 - q_i \varepsilon_i \bar{W}_i) \,, \tag{7}$$

where

$\prod_{i}^{n}$ = product of terms "i" to "n,"

n = number of gamma or x-rays in coincidence with the gamma ray of interest.

i = identification of the coincidence photon of interest,

q_i = fraction of coincidence photons "i" in coincidence with the gamma ray of interest,

ε_i = total detection efficiency of the coincidence photon "i,"

$\bar{W}_i$ = angular correlation factor between the photon of interest and the "i"th coincidence photon.[2]

The angular correlation factor is often approximated as one or is assumed to be equal to one when the angular correlation coefficients are not known. This correction should be multiplied by the net FEP count rate to obtain the corrected FEP count rate.

Some representative total detection efficiencies are given in Figure 5. Correction factors for coincidence summing for several gamma rays emitted in the decay of $^{152\&}$Eu, ^{60}Co, and ^{88}Y are given in Table 5.

The absolute FEP efficiency ε is determined by

$$\varepsilon = C/N_\gamma \,, \tag{8}$$

where

C = net count rate of the FEP,
N_γ = gamma ray emission rate of the calibration standard.

The gamma-ray emission rate N_γ of the calibration standard is reported as nuclear disintegration rate, which can be calculated by

$$N_\gamma = ND \,, \tag{9}$$

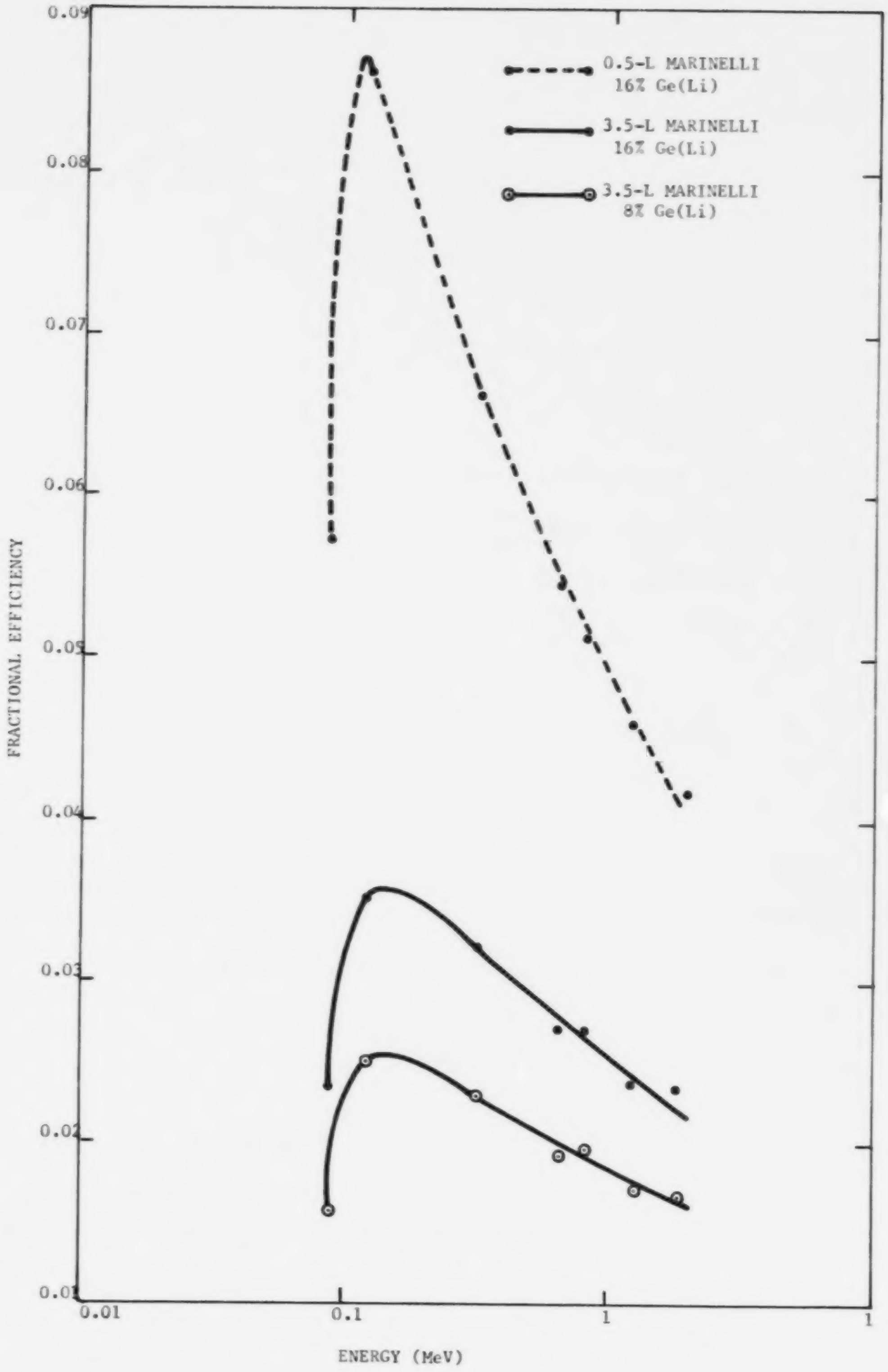

Figure 5. Total detection efficiency.

TABLE 5. CORRECTION FACTORS FOR COINCIDENCE SUMMING

Nuclide	Energy (keV)	Detector 1 (3.5-L)[a]	Detector 3 (3.5-L)[a]
^{152g}Eu	121.8	1.02	1.03
	244.5	1.03	1.04
	344.2	1.01	1.02
	411.1	1.03	1.05
	444.0	1.03	1.04
	779.1	1.02	1.03
	964.2	1.01	1.02
	1086.0	1.00	1.00
	1112.2	1.01	1.02
	1408.1	1.01	1.02
^{60}Co	1173.2	1.02	1.03
	1332.5	1.02	1.03
^{88}Y	898.0	1.02	1.02
	1836.1	1.02	1.03

---

[a] See Section 4.2, Table 1, for specifications for the detectors.

where

N = number of photons of a given energy emitted per nuclear decay (i.e., the branching fraction),
D = disintegration rate of the calibration standard.

Log-log plots of efficiency data, with energy as the ordinate and efficiency as the abscissa, can be used to display a wide range of energies. These plots show a fairly linear curve above about 150 to 300 keV for most germanium detectors. Several typical curves for calibrations for aqueous Marinelli beaker geometries are shown in Figure 6. The decrease in efficiency shown at low energies is caused by absorption of photons by the sample matrix, cryostat endcap, and the dead layers of the detector itself. The gradual decrease in efficiency at higher energies occurs because of the reduction in the cross section for interaction of the detector material (e.g., germanium) with increasing energy of the incident photon.

4.4.2.5 Analytical Efficiency Expressions

When efficiency data are available for a sufficient number of energies in the energy region of interest, a method of representing the efficiency as a function of energy must be chosen. Graphical methods can be used; however, it is often desirable to express the efficiency in some analytical form as a function of gamma-ray energy. Such expressions can be readily programmed and are adaptable to automatic data analyses.

Least-squares fitting procedures are used to fit the efficiency data to an analytical expression. Such a technique has the advantage of yielding an unbiased estimate of the fitting errors. However, the analytical expressions must be carefully selected to avoid introducing systematic divergences from the observed data.

Several semi-empirical formulas involving the physical characteristics of the detector have been proposed[66-70] to fit germanium detector efficiency curves. Due to incomplete charge collection, local variations in efficiency,[71] and uncertainties in the actual geometry of coaxial and closed-end coaxial detectors, empirical analytical functions are often preferred.[63,72] Table 6 lists some proposed empirical analytical functions with appropriate literature references for each expression. The energy ranges over which these functions give adequate fits can be found in the listed references or in the review papers of McNelles and Campbell[72] or Singh.[73] When the available degrees of freedom are sufficiently large (i.e., the number of data points should exceed the number of fit parameters by at least one, preferably more), the data can be broken into two separate regions for fitting, if fitting the data for one extended region leads to systematic divergences.

All the expressions shown in Table 6 are similar, and several are special cases of the more general equations. The simple log-log fit (entry number 1 in Table 6) can produce reasonable results in the 300- to 1800-keV region for many detectors. Figure 7 illustrates the deviation of three detectors from this analytical form. The reduction

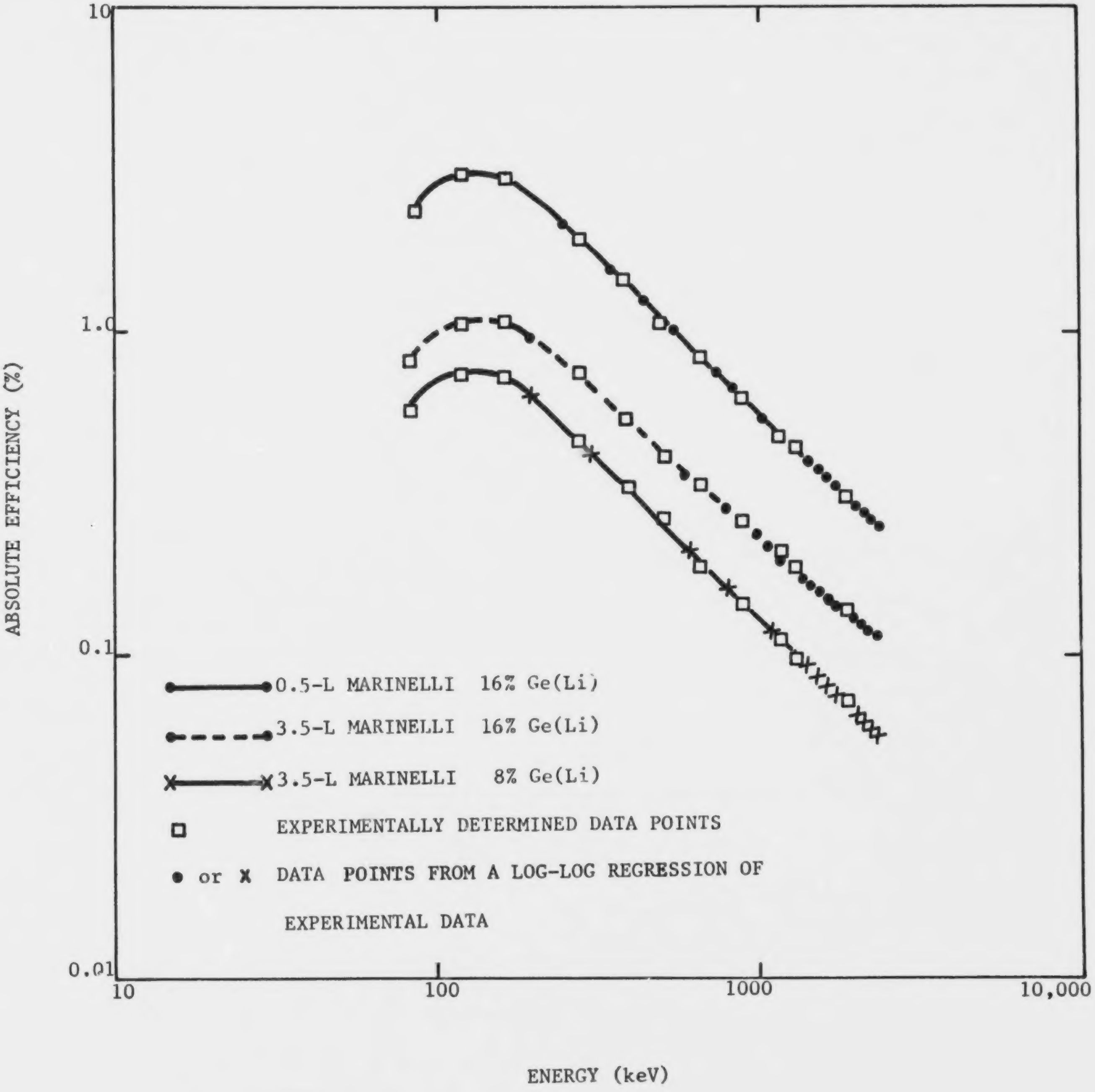

Figure 6. Typical absolute FEP efficiency curve.

TABLE 6. ANALYTICAL FUNCTIONS USED TO FIT EFFICIENCY DATA FOR GERMANIUM DETECTORS

Function/formula	References
$\ln \varepsilon = a_1 + a_2 \ln E$	48
$\ln \varepsilon = a_1 \ln \left(\frac{1.022}{E}\right) + a_2 \ln \left(\frac{1.022}{E}\right)$	74
$\ln \varepsilon = a_1 + a_2 \ln E + a_3(\ln E)^2$	75
$\ln \varepsilon = a_1 \ln E + a_2(\ln E)^2 - a_3/E^3$	76
$\ln \varepsilon = \sum_{j=1}^{n} a_j(\ln E)^{j-1}$	27
$\varepsilon = a_1 \exp(a_2E) + a_3 \exp(a_4E)$	77
$\varepsilon = (a_1/E)^{a_2} + a_3 \exp(-a_4E) + a_5 \exp(-a_6E) + a_7 \exp(-a_8E)$	72
$\ln \varepsilon = a_1E^{-3} + a_2E^{-2} + a_3E^{-1} + a_4 + a_5E$	47
$\ln \varepsilon = a_1 + a_2E + a_3E^2 + a_4E^3 + a_5E^4 + a_6E^5$	78

where

$\ln$ = natural log,

exp = exponential function,

ε = absolute FEP efficiency,

$a_1, a_2, a_3, \ldots$ = fit parameters.

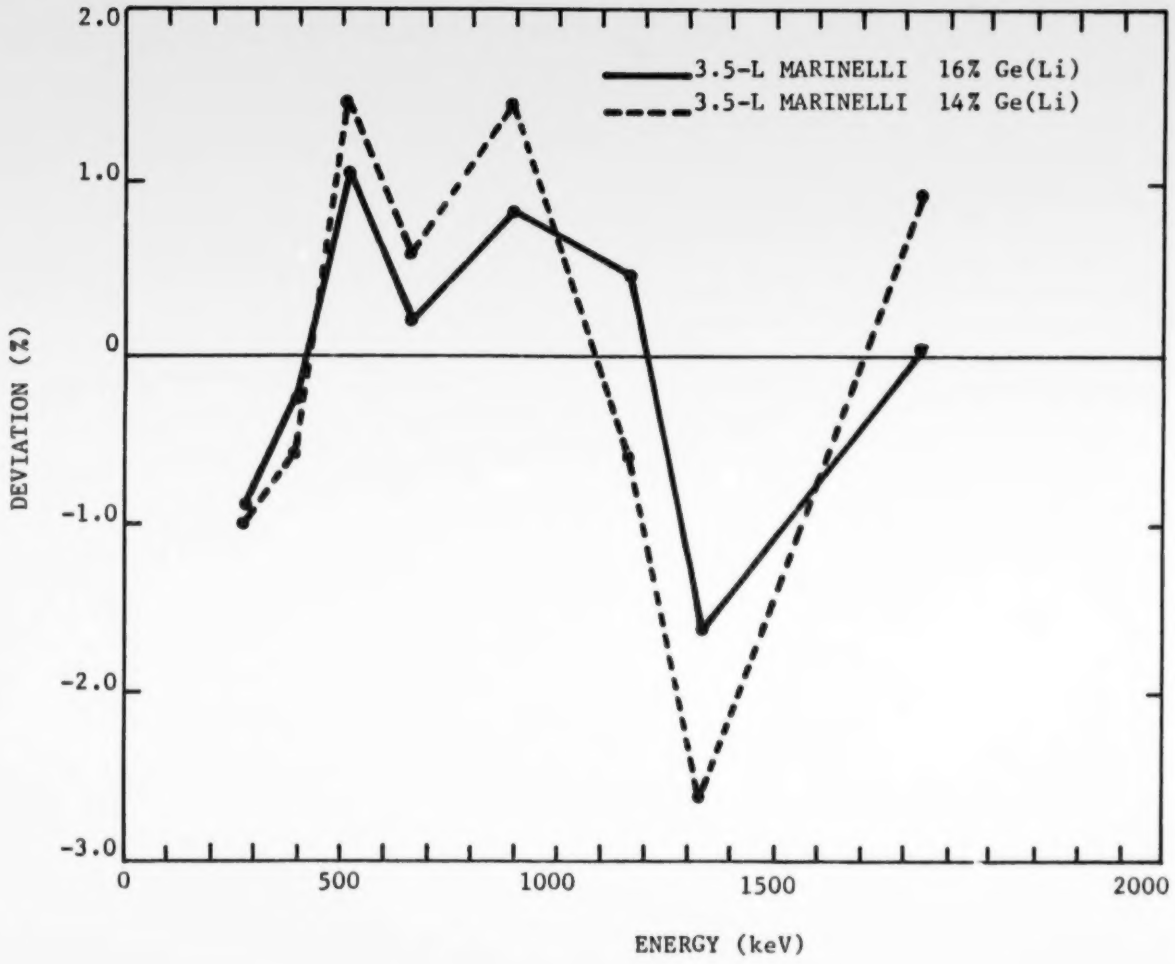

Figure 7. Deviation of log-log fit from experimental efficiency.

in efficiency observed at lower energies is often difficult to represent with any analytical function. Several of the terms (e.g., the $-a_3/E^3$ term in the fourth expression) in the analytical functions shown in Table 6 have been added to improve fits of the data in the lower energy region.

SECTION 5

DATA ANALYSIS

5.1 SPECTRAL ANALYSIS

Most routine analysis of gamma-ray spectra from germanium systems is performed with the aid of computer-automated techniques. Automated techniques of spectral analysis can handle a large volume of spectra rapidly, thereby reducing manpower costs and producing cost-effective data reduction despite high initial investment in equipment and manpower. Software for automated spectral analysis can be developed by the users, adapted from published routines, or bought from commercial suppliers of nuclear equipment.

Most programs for automated analysis include two phases: peak analysis and radioisotope identification.[79] Peak analysis usually includes procedures for spectral smoothing, peak locating, and peak fitting. Features for eliminating pseudopeaks and calculating the energy and gamma-emission rates of the FEP are also generally included in this phase. Peak analysis software typically compiles a table of FEPs found in the spectrum, gamma emission rates of the FEPs, estimates of statistical uncertainty of the emission rates, and a list of pertinent fitting parameters determined for each FEP. The peak fit information and the estimates of statistical uncertainty can be used to evaluate the overall accuracy of the calculated gamma-emission rate.

In the second phase, the isotope identification, the individual radionuclides present in the spectrum of the sample are identified and their activities on the date of sample collection are calculated. This phase is often set up for automatic generation of reports for use in fulfilling regulatory requirements. After an analysis program is selected, the user should continually review new or modified methods of analysis to ensure that the methods used meet changing analytical requirements in the most cost-effective manner.

Several aspects of spectral analysis should be considered when selecting an analytical technique for data reduction of germanium spectra. Our discussion emphasizes automated techniques because of their prevalence, but all the methods described can be adapted to manual analysis of data. This discussion is not intended to be an exhaustive report of all available techniques for analysis of data; however, it will serve to introduce the most commonly used techniques.

5.1.1 Spectral Smoothing

Due to the statistical nature of the nuclear disintegration and detection processes, the counts C in each channel of a spectrum can have a statistical fluctuation of the order $\sqrt{C}$. These statistical fluctuations tend to produce a quite irregular spectrum, which can often present problems when trying to locate peaks. Effective spectral smoothing can reduce these statistical fluctuations; however, the smoothing process must not shift the centroid of the peak appreciably or alter its area significantly.

Techniques for spectral smoothing[14,80,81] and methods using Fourier transform[82-84] have been applied to germanium spectra. The more sophisticated programs for gamma-ray spectral analysis smooth the data before trying to locate or fit peaks, whereas other programs smooth the data as an integral part of the peak location.[27,79,85-88]

Techniques for smoothing data that use Fourier transform methods have been reported,[82-84] but this approach has yet to be recognized as a routinely acceptable technique. Inouye, Harper, and Rasmussen[82] reported good results on a wide variety of gamma-ray spectra, some very complex. Inouye[83] has used a square-root transform to filter out statistical fluctuations. Tominaga, Dojyo, and Tanaka[84] investigated the effect of Gaussian-shaped digital filters on determination of the area of a peak. The application of Fourier transforms to gamma-ray spectral analysis should be studied more extensively before such a technique is adopted. This technique may be quite expensive in terms of computer time unless the recently developed Fast Fourier Transform algorithms are used.

The most commonly used method for smoothing fluctuating data is the method of moving averages. Weighting factors can be chosen which are exactly equivalent to those one would use for a least-squares fit of the data to a polynomial. Weighting factors also can be chosen which convolute the points into a smoothed, "n"th-order derivative. Savitzky and Golay[14] provide an excellent discussion of smoothing and differentiating data; they also tabulate the convolution integers for many cases.

Figure 8 shows (1) part of an unsmoothed germanium spectrum, (2) the smoothed spectrum fit to a quadratic or cubic polynomial, (3) the smoothed first-derivative fit to a quadratic polynomial, (4) the smoothed first-derivative fit to a cubic polynomial, and (5) the smoothed second-derivative fit to a quadratic or cubic polynomial. The convolution integers for smoothing and for the smoothed second derivative are the same for a quadratic and cubic least-squares fit. Table 7 lists the data from which Figure 8 was plotted.

The smoothed data for a quadratic or cubic function, S_i, the first derivative for a quadratic function, D_i (quad), the first derivative for a cubic function, D_i (cub), and the second derivative for a quadratic or cubic function, D_i^2, for a five-point smoothing process are calculated by

$$S_i = (1/35)(-3C_{i-2} + 12C_{i-1} + 17C_i + 12C_{i+1} - 3C_{i+2}) \; ; \qquad (10)$$

$$D_{i\ (\mathrm{quad})} = (1/10)(-2C_{i-2} - C_{i-1} + 0C_i + C_{i+1} + 2C_{i+2}) \; ; \qquad (11)$$

$$D_i\ (\mathrm{cub}) = (1/12)(C_{i-2} - 8C_{i-1} + 0C_i + 8C_{i+1} - C_{i+2}) \; ; \qquad (12)$$

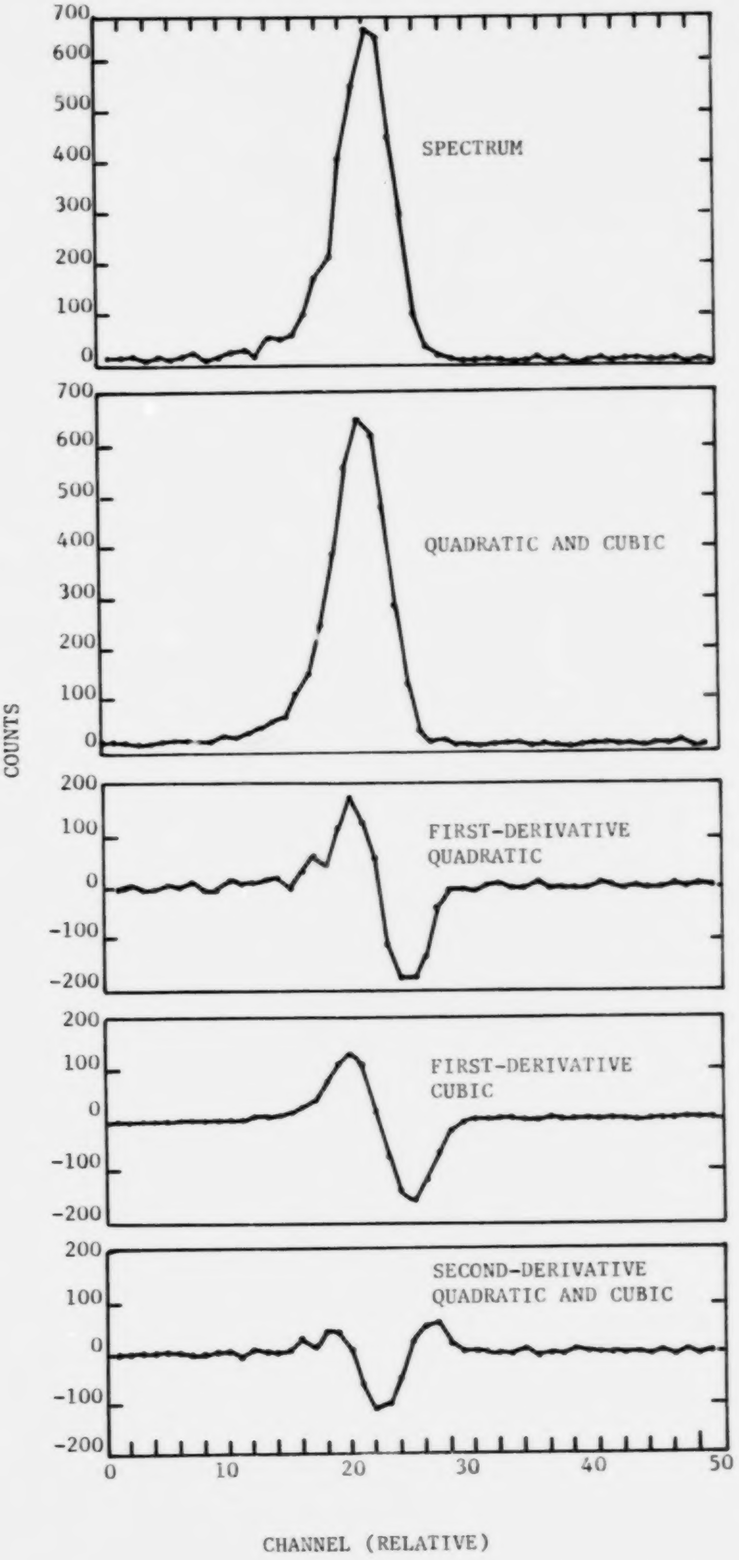

Figure 8. Effect of spectral smoothing and differentiation on a typical FEP.

TABLE 7. EFFECT OF SPECTRAL SMOOTHING AND DIFFERENTIATION ON A TYPICAL FEP

Channel (relative)	Raw data (counts)	Smoothed data (quadratic or cubic)[a]	First derivative (cubic)[a]	First derivative (quadratic)[a]	Second derivative (quadratic or cubic)[a]
1	13	12.91	1.29	-4.08	-0.71
2	10	12.99	-1.50	2.74	-1.00
3	16	11.11	-0.59	-2.58	0.28
4	6	10.88	-0.59	-2.58	-0.28
5	12	8.48	-0.29	2.24	2.71
6	9	10.62	3.09	-0.58	1.57
7	13	14.79	0.59	8.24	-1.99
8	21	15.77	0.59	-3.08	-2.57
9	9	13.19	1.50	-5.58	2.99
10	14	13.91	2.89	9.41	5.28
11	24	23.65	3.39	8.49	-4.85
12	28	22.42	7.69	-6.74	5.57
13	19	31.51	7.50	15.99	3.28
14	55	42.05	9.49	16.58	0.14
15	48	52.62	17.39	-2.99	4.57
16	61	62.02	28.69	26.99	25.57
17	103	107.02	44.39	59.41	12.57
18	171	151.79	80.79	45.66	39.99
19	215	247.57	112.59	121.66	41.42
20	409	389.19	129.79	181.08	10.00
21	547	556.59	110.09	127.66	-62.99
22	654	651.59	18.79	60.16	-109.99
23	643	619.77	-68.89	-112.24	-99.57
24	455	479.51	-142.89	-181.99	-46.71
25	302	281.68	-154.69	-179.91	28.71
26	110	130.65	-112.99	-137.08	55.14
27	42	37.79	-66.39	-36.08	59.99
28	20	19.05	-22.89	-9.58	20.14
29	15	13.19	-8.49	-4.24	5.00
30	9	8.65	-2.99	-5.83	3.14

TABLE 7 (continued)

Channel (relative)	Raw data (counts)	Smoothed data (quadratic or cubic)[a]	First derivative (cubic)[a]	First derivative (quadratic)[a]	Second derivative (quadratic or cubic)[a]
31	5	6.88	-1.09	1.16	2.71
32	10	8.28	0.00	2.83	-0.28
33	9	9.08	0.29	-2.24	-1.28
34	7	6.99	1.09	-1.16	2.99
35	8	10.48	0.29	6.25	-1.28
36	16	11.11	0.39	-1.58	-1.71
37	6	10.88	-1.59	-3.58	-2.28
38	10	6.14	-2.50	-1.08	1.85
39	3	5.05	0.69	-3.83	2.14
40	5	6.11	0.29	6.25	1.28
41	12	8.74	1.79	0.66	-1.14
42	7	10.17	0.50	-0.91	-1.57
43	11	8.77	-0.69	1.00	0.42
44	8	9.19	-0.29	-1.99	-1.00
45	8	7.05	0.09	-0.75	2.14
46	7	8.88	0.39	2.66	-0.28
47	12	9.25	0.89	0.33	0.14
48	8	10.74	0.39	-0.16	-1.14
49	12	9.85	-0.50	0.91	0.14
50	9	10.37	-0.69	-1.83	-1.57

[a] The function in parentheses is the type of polynomial used in the least-squares fit.

$$D_i^2 = (1/7)(2C_{i-2} - C_{i+1} - 2C_i - C_{i+1} + 2C_{i+2}) \quad , \tag{13}$$

where

C_i = number of counts in channel "i,"

i = running index of the channel number in the original data table.

The convolution integers and the normalization integers are taken from Savitzky and Golay,[14] and the correction on the second-derivative convolution integers are taken from Quittner.[11]

Yule[81] noted that the tops of photopeaks are roughly quadratic and the sides are roughly cubic, which suggests that quadratic or cubic polynomial smoothing constants can be chosen. Fortunately, the weighting factors for a least-squares fit to quadratic and cubic polynomials are identical. Yule[80,81] also found that the optimum number of channels to use in a smoothing process is equal to the number of channels in the FWHM of the FEP; the use of fewer channels will not produce adequate smoothing, and the use of more channels produces peak distortions.

To use the weighted, moving-average technique, the product of an appropriate weighting factor and the contents of the channel are summed for a selected number of consecutive channels; this sum is then divided by an appropriate normalization factor. The moving average is obtained by repeating the above process while advancing across the region of interest one channel at a time. In this process, the lowest energy channel is dropped from the region, and the next higher energy channel is added to the region to maintain a constant width. A (2m+1)-point smoothing process can be decribed by the general equation,

$$S_i = (1/N_m) \sum_{j=-m}^{+m} [(a_{m,j})(C_{i+j})] \quad , \tag{14}$$

where

S_i = smoothed value of channel "i,"

N_m = normalizing factor,

i,j,m = indices,

$a_{m,j}$ = convolution integer for channel "j,"

C_{i+j} = number of counts in channel c_{i+j} of the raw data (i.e., data before smoothing).

Yule[80,81] used different criteria to test the effectiveness of smoothing: (1) visual inspection of plots of the observed and smoothed data, (2) comparison of areas under the observed and convoluted results, (3) behavior of the smoothed first derivative, (4) statistical tests, and (5) the effect of multiple smoothings. Yule[80,81] found that the first four tests could not adequately detect small amounts of distortion;

therefore, the fifth test is used to magnify the distortion until it is detectable. In general, a single smoothing with the number of data points (channels) approximately equal to the FWHM of the peaks introduces negligible distortion. However, when overlapping peaks are present, distortion can be introduced. These conclusions indicate that smoothed data are preferred for locating peaks, but should not be used when determining areas of peaks if overlapping peaks are present.

Least-squares fitting methods, when applied to previously smoothed data, tend to extend the fitting width of peaks over the width determined when raw data are used. In other words, smoothing broadens the peak. Fitting width is defined as the region of data, representing a peak, on which a least-squares technique is applied. An equivalent result is obtained by a least-squares fit of unsmoothed data over a wider-fitting range.[84] Because smoothing data does not improve the least-squares fit and can obscure multiplet structure, unsmoothed data should be used to determine FEP areas.

5.1.2 Peak Location

Locating peaks by careful visual inspection of spectra can be time-consuming and dependent on subjective judgment. This dependency has led many authors to propose various methods for locating peaks with calculators and computers. Much emphasis has been placed on methods that are rapid and easily adapted to small, dedicated computers.

Three major methods, and variations of those methods, have been proposed for locating peaks: (1) location of maxima, (2) testing the smoothed first derivative, and (3) examination of second differences. Statistical tests can be used to confirm peaks after the spectra are treated mathematically. In the first method, locating peaks by finding maxima, the data are scanned until the contents of a given channel N satisfies the following conditions:

$$C(N - 2) < C(N) - S \sqrt{C(N)} \tag{15}$$

and

$$C(N) - S\sqrt{C(N)} > C(N + 2) \quad , \tag{16}$$

where

C(N) = contents of channel N,
S = sensitivity of the peak detector.

The factor S is chosen empirically; values of 1 to 1.5 have been reported to give good results.[89] This method has been used in a program called "INHOUD." Kemper and van Kempen[89] describe this program and provide Basic, Fortran, and Algol listings.

Wood and Palms[90] describe a program that uses a modification of this general approach. The spectrum is scanned channel by channel, and a peak is detected when

$$(1/3)\left[\sum_{i=0}^{2} C(n+i)\right] > (1/3)\left[\sum_{j=4}^{6} C(n+j)\right] + S\left\{(1/3)\left[\sum_{j=4}^{6} C(n+j)\right]\right\}^{1/2} , \qquad (17)$$

where

$C(n + i)$ = contents of channel $(n + i)$,
S = sensitivity of the peak detector.

The value of S is chosen empirically.

The procedure for locating peaks by finding maxima is easy to program, but often overlooks small peaks, identifies statistical fluctuations and other fluctuations in the spectra as peaks, and cannot separate multiplet peaks. This method of locating peaks can be augmented by rejecting (1) any peak that exceeds a certain width and (2) any peak with an area less than twice its standard deviation; these rejections reduce the number of pseudoFEPs detected.

Several authors [79,91-93] use the first derivative of the spectrum to locate peaks. The smoothed first derivative of a peak will show a maximum difference in slope at the points immediately to the left and right of the centroid of the peak. These points contain half as many counts as the peak centroid itself. The smoothed first derivative will have a value of zero at the peak maximum. A program can be written to detect groups of neighboring channels such that the smoothed first derivative D fulfills the criteria,

$$D(p) \le 0 \ , \qquad (18)$$

$$D(p + i) < 0 \qquad \text{for } i = 1, 2, \ldots, r \ ; \qquad (19)$$

and

$$D(p - i) > 0 \qquad \text{for } i = 1, 2, \ldots, \ell \ . \qquad (20)$$

The values of r and ℓ are chosen in accordance with the energy resolution so that significant peaks are recognized and statistical fluctuations are disregarded.[11]

Barnes[79] and Sasomoto et al.[91] suggest that statistical tests be performed on the derivative to ensure that only significant variations in the derivatives are processed. An example of the first derivative of a peak that has been fitted to a quadratic or cubic function is shown in

Figure 8. Yule[93] suggests that a fit to a quadratic function best locates the centroid of the peak; but Barnes[79] notes that, because there is no obvious choice between quadratic and cubic functions for locating single peaks and because the cubic function is more sensitive in detecting incompletely resolved doublets, the cubic function should be preferred.

The second derivative can also be used to find peaks. The second derivative of discrete data can be replaced by the second difference, defined by

$$D_N^2 = C(N + 1) - 2C(N) + C(N - 1) \ , \qquad (21)$$

where

D_N^2 = second difference at channel N,
$C(N)$ = contents of channel N.

Large fluctuations in the second difference, resulting from statistical fluctuation, Compton edges, and other irregular spectral features, are invariably present. Therefore, some form of smoothing procedure or other modification is required to identify peaks reliably. Mariscotti[85] proposed a method by which the data are smoothed "z" times over "w" channels to give the generalized second difference. This generalized second difference, $S_{z,w}(i)$, and its error, $\Delta S_{z,w}(i)$, are given by

$$S_{z,w}(i) = \sum_{j=i-zm-1}^{i+zm+1} C_{z,w}(i - j)Y(j) \qquad (22)$$

and

$$\Delta S_{z,w}(i) \approx \sqrt{Y(j)} \left\{ \sum_{j=i-zm-1}^{i+zm+1} [C_{z,w}(i - j)^2]^{1/2} \right\} \ , \qquad (23)$$

where

$C_{z,w}(i - j)$ = weighting factors for the "i"th term,
$Y(j)$ = contents of channel j.

A detailed study of the optimum selection of the averaging parameters w and z indicated that the best results are achieved when $w = 0.6\Gamma$ and $z = 5$, where Γ is the FWHM of the peak.[85] Mariscotti[85] used the condition $S_{z,w}(i) > f\Delta S_{z,w}(i)$, where f is a factor of confidence, to indicate a possible peak. Additional conditions, based on some distinctive peak characteristic, are used to eliminate pseudopeaks such as Compton edges and other irregular spectral features.

Routti and Prussin[86] use a modification of Mariscotti's second-difference procedure in the computer program SAMPO to perform automatic peak search. A smoothed second difference is calculated over (2k + 1) channels. The second difference S(i) and its standard deviation ΔS(i) are given by

$$S(i) = \sum_{j=-k}^{+k} C_j Y_{i+j} \tag{24}$$

and

$$\Delta S(i) = \left(\sum_{j=-k}^{+k} C_j^{\,2} Y_{i+j} \right)^{1/2} , \tag{25}$$

where

c_j = weighting factors for the "i"th term,
Y_{i+j} = contents of channel i+j.

The weighting coefficients are determined from the second derivative of a Gaussian. Optimum coefficients are chosen to maximize the ratio of the second difference to the standard error of the second difference. The weighting function may be varied to determine small peaks or components of multiplets more accurately. Peaks are located by comparing the statistical significance of the second difference [$SS(i) = S(i)/\Delta S(i)$] to given threshold values. An additional test is made on the shape of the peak before it is recorded as a valid peak.

Phillips and Marlow[87,88,94] use a modification of the smoothed second difference, which was first proposed by Robertson et al.[95] The search routine in their program, HYPERMET, uses a negative smoothed second difference, which is calculated by a sliding transform, often called a square-wave transform. The transform for an integer width M and its statistical variance are given by

$$KON(J) = \sum_{I=J-M}^{J+2M-1} [L(I)][K(I)] \tag{26}$$

and

$$VAR(J) = \sum_{I=J-M}^{J+2M-1} [L(I)]^2[K(I)] , \tag{27}$$

where

KON(J) = smoothed second difference of the Jth channel,
VAR(J) = variance in KON(J) for the Jth channel,
K(I) = number of counts in the Ith channel,
L(I) = -1 for $J-M \le I \le J-1$
= 2 for $J \le I \le J+M-1$
= -1 for $J+M \le I \le J+2M-1$.

The expected value of variance in KON(J) can be calculated simply by

$$\mathrm{VAR}(J) = 6M\bar{K} \tag{28}$$

where

M = width of the transform,

$\bar{K}$ = average of K(I).

A function, CONV(J) [= KON(J)/[VAR(J)]$^{1/2}$], can be used to detect peaks. This function is normally distributed about zero with unit standard deviation, except in the vicinity of a peak or other sharply varying feature with a width of the order of M. When the function of CONV(J) exceeds a certain threshold value, usually 4, a peak is identified. Due to the width of the onset of Compton edges, the function CONV(J) is found to be insensitive to Compton edges; thus, further discrimination based on peak shape, which is necessary in most routines when generalized second difference is used to locate peaks, is not needed.

When the threshold value for peak detection is set below 4, a rectangular wave is used to detect peaks. The rectangular-wave transform can be written

$$\mathrm{KON}(J) = \sum_{I=J-2M}^{J+3M-1} [L(I)][K(I)] \quad , \tag{29}$$

where

$$\begin{aligned} L(I) &= 1 \text{ for } J-2M \le I \le J-1, \\ &= 4 \text{ for } J \le I \le J+M-1, \\ &= -1 \text{ for } J+M \le I \le J+3M-1, \end{aligned}$$

and all other parameters are as defined previously. The rectangular-wave transform is more sensitive than the square-wave transform for detecting a weak peak on a high background.

Phillips and Marlow[87,88,94] performed a detailed comparison of four transforms: (1) square wave, (2) rectangular wave, (3) covariance calculated by means of a zero-area Gaussian, and (4) second derivative of a Gaussian using an optimum width. The zero-area Gaussian was determined to be best, but the rectangular-wave transform was nearly as effective. Performance of the transforms on gamma-ray spectra with poor statistics was tested in detail.

The great advantage of the square- and rectangular-wave transforms is that the calculations can be accomplished by computing devices in fixed-point arithmetic, which is an efficient and rapid calculating mode. This is of considerable value because of the increased application of dedicated mini- or microcomputers to data acquisition and processing. Several other methods of detecting peaks have been described in the literature,[11,27,96,97] but none has been used as widely as the procedures described above. In general, the square- or rectangular-wave transforms should be adequate for most environmental applications. If greater detail about a particular method is required, the reader should refer to the original literature as referenced in this section.

5.1.3 Peak Intensity and Peak Centroid Determination

In analyzing gamma-ray spectra of environmental samples, the ultimate task is to measure the FEP intensity accurately. Many specific approaches to determining FEP intensity have been developed from two techniques--nonfitted methods and fitting methods.

The FEP intensity can be determined directly from the counts in the channels of the peak by some form of summing or weighted summing of the counts in each channel. When this method is used, the background is generally estimated from several channels within the peak or in the vicinity of the peak. This technique can be termed determination of peak area by nonfitted methods.

A second method of determining the intensity of an FEP uses a computer or programmable calculator to fit the peak to a function before determining the area and centroid of the peak.

A detailed account of each method is beyond the scope of this report and would be of limited value because comparisons of the methods by various authors have yielded conflicting results.[98-101] However, a brief description of each method may be of value in selecting a method for data analysis or to understand better the advantages and limitations of a previously selected method.

5.1.3.1 Nonfitted Methods

Most nonfitted methods can be adapted for hand calculation or readily programmed on a calculator or small computer. These methods have particular merits and drawbacks; of particular note is the fact that nonfitted methods are capable of processing only singlet peaks. Fortunately, many types of environmental samples have spectra with few multiplets. The difficulties encountered as a result of the inability of these methods to resolve multiplets quantitatively should be considered in light of the relative number of multiplets that will be encountered in the routine samples of a laboratory.

Several authors have identified and compared various nonfitted methods of peak analyses.[98,99,102] Seven basic nonfitted methods of determining areas of peak have been proposed and used in different laboratories:

1. Total peak area (TPA) method

$$A = \sum_{i=\ell}^{r} a_i - (r - \ell + 1)(a_\ell + a_r)/2 \quad , \qquad (30)$$

where

A = total net peak area,

ai = number of counts in channel "i",

ℓ = channel number at left limit of FEP,

r = channel number at right limit of FEP.

2. A modification by Wasson of the TPA method[98]

$$A = \sum_{i=-n}^{+n} a_i - (n + 1/2)(b_n + b_{-n}) \quad , \tag{31}$$

where

n = number of channels to the left and right limits of the FEP from the centermost channel,

bn = background in channel "n" as determined from a straight line drawn between channels "ℓ" and "r".

3. Covell's method[103]

$$A = \sum_{i=-n}^{+n} a_i - (n + 1/2)(a_n + a_{-n}) \ . \tag{32}$$

4. Sterlinski's method[104]

$$A = na_o + \sum_{j=1}^{n} (n - 2j + 1/2)(a_{-j} + a_j) \ . \tag{33}$$

5. A combination of the Wasson and Sterlinski methods[98]

$$A = na_o + \sum_{j=1}^{n} (n - j + 1)(a_{-j} + a_j) - \sum_{j=1}^{n} (j + 1/2)(b_{-j} + b_j) \ . \tag{34}$$

6. Quittner's method[105,106]

$$A = \sum_{i=-h}^{+n} (a_i - C_i) \ , \tag{35}$$

where

C_i = background in channel "i" as determined from a polynomial fitted to (2k + 1) channels on each side of the photopeak

$$C_i = p_\ell + q_\ell(X_p + i - X_L) + \left[\frac{3(p_r - p_\ell)}{M^2} - \frac{(q_r + 2q_\ell)}{M}\right](X_p + i - X_L)^2$$

$$+ \frac{2(p_\ell - p_r)}{M^3} + \frac{(q_r + q_\ell)}{M^2} (X_p + i - X_L)^3 \quad (36)$$

where

X_L and X_R = center channel of the regions described by the left and right polynomials, respectively ($X_L = \ell - k$, $X_R = r + k$),

Xp = centermost channel,

Pℓ and pr = values of the polynomials at XL and XR,

qℓ and qr = slopes of the polynomials at XL and XR ,

M = XR - XL .

7. A combination of the Sterlinski and Quittner methods[98]

$$A = na_o + \sum_{j=1}^{n} (n - j + 1)(a_{-j} + a_j) - \sum_{j=1}^{n} (j + 1/2)(C_{-j} - C_j) \quad (37)$$

and

$$A = \sum_{i=\ell}^{r} (a_i - b_i) ,$$

where

a_i = contents of channel "i,"

ℓ = left point at which the measured and the baseline spectra intersect,

r = right point at which the measured and the baseline spectra intersect,

b_i = counts calculated for the baseline spectra at channel "i."

The various experimental conditions (peak separation, peak-to-background ratio, and peak broadening due to high count rate and instrument drift) are so complex that no method of determining the peak area can be clearly shown to be superior to all other techniques under all conditions. The different conclusions drawn by Hertogen et al.[99] and Baedecker[98] serve to emphasize this point. The many options investigated by Hertogen et al.,[99] such as the channel width used in determining the peak area or in determining the background, also indicate the complexity involved in comparing various techniques. Nevertheless, a qualitative comparison of the techniques is worthwhile.

All the techniques proposed (other than the TPA method) attempt either to minimize the effects of statistical fluctuations on the peak or improve the estimation of the baseline (background).

The TPA method obtains the full area of the FEP by summing and determines the background from a straight-line fit to a continuum channel or an average of several channels on each side of the FEP. This technique is readily adaptable to either hand or computer calculation. Errors in estimating the net area due to peak broadening are less than those from any other technique listed above; however, the technique sums over a region of channels that add considerably to the error of the peak integration, but add little to the net number of counts. The results are not strongly influenced by statistics when the FEP is relatively intense and the background is not excessive, but are subject to large statistical fluctuations for weak peaks on high backgrounds. The Wasson[98] modification of the TPA method excludes those channels in the wings of the FEP that add considerably to the error of peak integration while adding little to the net number of counts. The Wasson technique will yield greater errors when peak broadening has occurred.

Covell[103] based his method on the fact that a summation over a fixed portion of the FEP bears a constant proportionality to the total area of the FEP. The method is simple to program or calculate by hand, but is subject to errors from statistical fluctuations and peak broadening. The consistency and accuracy of the results of this method depend on optimum selection of peak boundaries. Heydorn and Lada[107] found that the optimum integration limits on each side of the centroid are a function of the peak-to-background ratio and correspond to about 0.91 FWHM on either side of the peak for those peaks that are small relative to the background.

Sterlinski[104] modified Covell's method to give increasingly greater weight to those channels that have an increasingly greater number of total counts. The variance of either Covell's or Sterlinski's method is increased because the summation is carried out with the use of a relatively high baseline, rather than one drawn across the base of the FEP.[98]

The Wasson-Sterlinski[98] technique uses the advantage of the Sterlinski approach: It gives increasingly greater weight to those channels that have an increasingly greater number of total accumulated counts and eliminates the increased variance of the Sterlinski technique resulting from the high baseline.

Quittner[105,106] attempted to improve the estimation of the baseline by fitting a polynomial to several points on the left and right of the peak. This technique gives a good representation of the background for weak peaks, or peaks near the Compton edge, but requires several background channels, usually at least five, on the left and right of the peak.

The Ralston and Wilcox[108] technique, which uses an iterative method to construct the baseline, yields precise results, but gives a systematically lower baseline.[105] The low baseline will lead to large errors when evaluating small peaks superimposed on large backgrounds or Compton regions.[105]

Baedecker[98] found that the methods of Covell and Sterlinski showed poorer precision than other methods of peak analysis, due perhaps to the sensitivity of these two methods to loss of resolution or shifting of the peak. The TPA method was found to be less precise than the Wasson, Wasson-Sterlinski, Quittner, or Sterlinski-Quittner methods.[98] After comparing the four techniques, Baedecker[98] and Hertogen et al.[99] concluded that Quittner's method gave better results for peaks with small peak-to-background ratios; however, this method gave poorer results when the polynomial could not be fitted accurately because of an inadequate number of background channels on either side of the peak. The Ralston-Wilcox method gave systematic errors when the peak-to-background ratio was low.[99] Hertogen et al.[99] found that errors in the calculated area of the peak as a function of decreasing peak-to-background ratio were not biased for most methods and did not increase rapidly with decreasing peak-to-background ratio. These conclusions are very reassuring for applications in environmental analysis.

Most methods could be applied to environmental analysis. The advantage of the Quittner method is its good performance for small peak-to-background ratios. However, the results of a spectrum analysis must always be carefully scrutinized by an experienced spectroscopist, regardless of the technique used.

The TPA method is often used as a back-up method or as a semi-quantitative check on other methods; therefore, three computer programs[89,90,109] based on this method are described briefly.

All three computer programs locate the channels beginning and ending the peak by statistical tests. The backgrounds are estimated by a straight line drawn between the average of several channels on the right and left of the peak. The centroid of the peak is located by various methods. One computer program locates the centroid of the peak to the nearest half-channel (statistical fluctuations will decrease the accuracy of this method) by choosing the channel with the largest number of stored counts as the location of the centroid of the peak.[89] Other programs locate the centroid from its first moment M, given by

$$M = (1/A) \sum_{i=L}^{R} iN_i \ , \qquad (38)$$

where

A = net counts in the peak,

L and R = channel numbers assigned as the left and right limits of the FEP,

Ni = net counts (counts after the background has been subtracted) in channel "i."

The centroid can also be located by estimating the channel number at which the first derivative of the data changes sign.

The variance V for the TPA method is given by

$$V = \sum_{i=\ell+1}^{r-1} A_i + [(r - \ell + 1)/2]^2 (A_\ell + A_r) \quad , \qquad (39)$$

where all terms are as defined previously. The variance for each method can be found in the reviews and references listed above or evaluated by using standard techniques for propagation of error (see Ref. 110).

5.1.3.2 Fitting Methods

Many approaches to fitting an FEP are described in the literature. Essentially, all approaches fit some analytical function, most often a Gaussian function, to the FEP by means of a least-squares technique. The forms of the analytical function and the methods for obtaining the least-squares solution are numerous.

Several analytical functions and least-squares techniques for fitting have been chosen for either simplicity[111-113] or performance of a specialized task.[114-117] Much recent work in this area has been concerned with adapting both the fitting functions and fitting processes for use on small computers.[112,113,118] Some adaptations sacrifice accuracy to increase the speed of processing and to reduce the amount of computer memory required.

5.1.3.2.1 Fitting Functions

The FEP generated by a germanium detector has a predominantly Gaussian shape with a tail on the low-energy side. A Gaussian function is described by

$$Y(X) = A \exp[(Xp)^2/(2\sigma^2)] \quad , \qquad (40)$$

where

$Y(X)$ = amplitude of the Gaussian at channel X,

X = channel number,

A = height of the Gaussian,

p = centroid of the Gaussian,

σ = width of the Gaussian (FWHM = 2.355σ).

The Gaussian shape of the germanium FEP results from the statistical spread of the electron-hole pair energies generated in the germanium detector. The noise of the electronics system further broadens the FEP. The tail on the low-energy side of the FEP results from the trapping and recombination of charges, escape of electrons from the sensitive volume of the detector, and Compton scattering into the detector from surrounding material. The FEP also may exhibit a tail on the high-energy side of the peak, which results from pulse pile-up at high count rates, improper pole-zero cancellation, or gain-stabilizer effects. However, this tail can usually be eliminated by proper adjustment of the instrument.

The true shape of the peak generally is approximated by using an analytical function containing variable parameters. These shape parameters then can provide an easy method for characterizing (i.e., obtaining the area and the centroid of) a peak. Obviously, the results obtained from fitting the function are most trustworthy when the analytical function reproduces the experimentally observed shape.

Many different functions have been used to represent spectral peaks (Table 8). The exact equation for a particular functional form can be obtained by referring to the appropriate reference listed in the table.

The functional representation of the FEP should be as simple as possible while still describing the peak well. More complex functions tend to require more computer memory and computation time, while often tending to diverge, oscillate, or converge to spurious optimal solutions. This last problem can be minimized by placing appropriate constraints on the fitting parameters.[121]

In general, the complexity of the analytical function and the complexity of fitting the function increase directly with the number of fitting parameters used. For this reason, the number of fitting parameters is held to a minimum and is either constrained (held to maximum or minimum values relative to their initial values)[87,88] or held constant for an FEP of a certain energy.[27,86,117,124,127]

Routti and Prussin[86] were the first to use parameters with fixed values. They selected well-isolated, intense peaks to determine values for these fixed parameters by a process termed peak-shape calibration. The values are usually determined from peaks within the actual spectrum or are determined for a given spectroscopy system and used for all subsequent analyses. Determining the parameter values within the actual spectrum or varying the values with constraints should yield the best results because a spectroscopy system is often not completely stable from sample to sample. However, determining the parameter values from the actual sample spectrum requires more computation time and may require more intervention by a knowledgeable spectroscopist than would be required if the values were known from previous measurement and held constant during the fitting process. Gunnink and Niday[27] and Phillips and Marlow[87,88] present a good discussion of the calibration of peak shapes and optimization of the values of peak-shape parameters.

TABLE 8. FITTING FUNCTIONS

Functional description	Number of fitting parameters	References
Simple Gaussian	3	85, 118-123
Two Gaussians (same width)	4	100
Gaussian with an exponential tail on the low-energy side	4	100-102
Two Gaussians (independent widths)	5	100
Gaussian plus exponential tails on low- and high-energy sides	5	86
Gaussian plus exponential and error functions on the low-energy side	6	100, 124
Gaussian plus a complex exponential tailing function	6	27, 125
Gaussian with an exponential tail and a dual exponential function to describe the continuum	6	91, 101
Gaussian plus a dual exponential tail on the low-energy side and an exponential function on the high-energy side	7	78, 79, 87, 88, 121
Skewed Gaussian with a constant tail and an exponential tail on the low-energy side	8	100, 126
Two Gaussians with an arc-tangent function and a constant on the low-energy side	8	100, 101, 117

When peak-shape calibration is used, only the position, the amplitude, and possibly the width of the peak are allowed to vary. Most fitting programs hold all values constant except the position and height for each component of a multiplet peak. This increases the number of fit parameters by two for each additional component of a multiplet peak.

In addition to attempting to locate components of multiplet peaks in the peak search routine, most sophisticated programs test the goodness of the FEP fit (i.e., check the residuals of the fit) to find additional weak or ill-defined components within a peak or group of peaks.

A practical consideration, often overlooked, in obtaining a good-quality fit is that the number of points in the FEP, not including background channels, must be greater than the number of free (nonconstrained) parameters in the fitting equation.[122] This may require many channels within the FEP when peak-shape calibration is not used or when complex analytical functions are used. An energy calibration of about 0.5 keV/channel will produce an adequate number of channels in the FEP if peak-shape calibration is to be used.

Extra terms are generally added to the functions to account for background contribution to the shape of the FEP. The functions have varied from the simple assumption of a constant background to the complex treatments of adding a third-order polynomial or an exponential term to the shape function. A quadratic function has been the most frequently used method of compensating for the background contribution,[87,88,124,127] with a cubic function also being used often.[117,126] Quadratic and cubic polynomials generally give superior results if the slope of the background within the spectrum varies rapidly.[105,106,126] The most common cause of rapid background variation is superimposition of the FEP on a large Compton or beta continuum.

Several authors have evaluated the effects of fitting functions on the results of FEP analysis.[100,101,121] McNelles and Campbell[100] place the functions into three classes: (1) simple forms (entry number 1 in Table 8), (2) forms using one-component tailing (entry numbers 2 through 5 in Table 8), and (3) forms using two-component tailing (entry numbers 6 through 11 in Table 8). They found that the functions using two-component tailing gave the best fit. Results of a study by Lederer[121] agree with those of McNelles and Campbell,[100] whereas Takeda et al.[101] concluded that the functions did not differ significantly. Takeda et al.[101] did find a difference of 5 to 10 percent in the determined areas of the peaks; however, no systematic tendency was observed. This variation in peak areas does subject the conclusion of Takeda et al.,[100] that all fitting functions evaluated were equally accurate, to question. Some comparisons of the various fitting functions and data to establish their validity are described in the references listed in Table 8.

In general, comparisons of fitting functions and the data used to test the performance of the functions have used strong peaks and/or weak backgrounds.[100,101,121] Phillips and Marlow[94] tested their fitting function on spectra with very poor counting statistics similar to those often encountered in environmental applications. Their functions gave good results for such peaks, but the weighting scheme normally used in the least-squares analysis showed a definite trend toward smaller-than-actual areas for the peaks and an increased fluctuation in mean position of the peak.

In the usual weighting procedure, where weights are set equal to the reciprocal of the number of observed counts, counts that are less than their expected value are given a larger weight than counts that are greater than their expected value. Therefore, the area of the peak is often underestimated. This underestimation may be serious for spectra in which many channels contain less than about 50 counts.[105] Phillips and Marlow[94] used a three-channel average for weighting purposes to remove the bias when the peak contained several channels with contents of less than 25 counts.

Differently shaped functions provide a variety of definitions of peak shape and, therefore, can produce a variety of different areas for a peak. These areas may be systematically biased if the experimental shape of the peak and the analytical function do not adequately agree. The systematic errors may be minimized when singlet peaks are considered if the efficiency calibration has been performed with the same shape function[48] that is used in the spectral analysis. However, this approach is not always adequate when multiplet peaks must be considered.

5.1.3.2.2 Least-Squares Methods

A nonlinear least-squares program usually is used to obtain the best estimates for the parameter values to be used in the fitting process. The least-squares procedure minimizes a function, χ^2, with respect to all chosen parameters simultaneously:

$$\frac{\partial}{\partial p_j} \chi^2 = \frac{\partial}{\partial p_j} \sum_{i=1}^{n} [Y_i - F_i(p_j)]/\Delta Y_i^2 = 0 \quad , \qquad (41)$$

where

Y_i and ΔY_i = measured value and error, respectively, at the "i"th data point χ_i,

Fi(pj) = value predicted by the function used in the fit.

The function χ^2 is considered to be a continuous function of the "n" number of parameters p_j describing a hyper-surface in "n" dimensional space. The least-squares process searches the hyper-surface for the actual minimum value of χ^2. This search is complicated by the fact that there are often local minima, besides the actual minima, for χ^2 within a reasonable range of values for the parameters p_j.[110]

Several methods have been formulated for performing the least-squares fit that have been used to the FEP: (1) the Gauss* method,

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*Also referred to as the Gauss-Seidel, Seidel, Gauss-Newton, Newton-Rapson, Taylor series, or linearization method.[121,128]

(2) the gradient-search or steepest descent method, (3) the variable-metric minimization or maximum-neighborhood method, and (4) the random-search method.

With the Gauss method, initial estimates of parameter values are put into a first-order Taylor series expansion to obtain a linear expression, which can, in turn, be treated by standard least-squares theory. The improved estimates are then returned through the process to obtain a more refined set of parameters. Programs using the Gauss method have been developed by Booth and Peterman,[129] Crosbie and Monahan,[130] Moore and Zeigler,[131] and Hartley.[132] The Gauss method has several drawbacks: (1) It may converge slowly, necessitating a large number of iterations; (2) it may oscillate wildly; (3) it may not converge at all; or (4) it may diverge.[110,128] However, if the initial estimates are in the immediate vicinity of the minimum value of χ^2, it converges relatively rapidly and reliably.

In the gradient-search or steepest-descent method, all values for the various parameters are incremented simultaneously, so that the relative magnitude of each parameter value is adjusted to give a resultant direction of travel on the hypersurface toward the direction of maximum change in χ^2.[110] This method will approach the minimum value of χ^2 rapidly, but in the vicinity of the minimum χ^2 value, it converges very slowly.[128] Marguardt[133] and Bevington[110] developed programs based on this method, and Spang[134] developed several modifications to the basic steepest-descent method.

The method of variable-metric minimization has been widely used.[86-88,122,127] In this method, an optimum interpolation between the Gauss method and the gradient-search method is performed to combine the best features of each. This technique was developed by Marguardt[135,136] and programmed by Davidon.[137] Beals[138] also developed a variable-metric routine. Phillips and Marlow[87,88] also use variable-metric minimization[139-141] with modifications by Fletcher.[142,143] The main advantages of the variable-metric method are rapid convergence near the minimum value of χ^2 and a relatively small amount of computer memory. Davidon's[137] formulation is slow because a relatively large number of tests and trial steps are used to check for convergence after each iteration. Fletcher's modification[142,143] greatly increases the speed of the program.[87,88]

The random-search method has been used by two authors[101,113] to optimize values of the fitting parameters. This method does not require good initial estimates of the fit parameters, and it converges rapidly without divergence or oscillation. The random-search technique was developed for computers that have a small memory allocation, but it requires longer computing times than other conventional fitting techniques.[113] This disadvantage may not be serious if the available computer is part of a P-MCA system, in which the program can be allowed to run in background mode while data acquisition is carried out in the foreground mode.

Several other methods or variations of these methods have been used or suggested for fitting an FEP.[100,112,118,121,123,126,144,145] The preceding discussion can be considered applicable to most of them.

Good initial values of the parameters used in a fit are essential for rapid, reliable convergence. Limiting the number of fitting parameters is also important for reliable results. Discussions of how to obtain good initial values of the fit parameters and methods of limiting the fitting parameters can be found in the references cited in Table 8.

Estimates of the statistical error in the net area of the peak and of the fitting error are required for assessing the overall error in estimating net counts in the FEP. The statistical error S (in percent) evaluated to one standard deviation is calculated by

$$S = (A_p + 2A_b)^{1/2}(100\%)/A_p \quad , \tag{42}$$

where

A_p = net area of the peak,
Ab = background underneath the peak.

Calculation of the error due to the least-squares fitting process is assumed to be the same for both the nonlinear and the linear case. The inverse of the generated square symmetric matrix containing the weighted derivatives of all the values of the parameters in the fitted function also forms an error matrix containing the variances and covariances of all values of the functional parameters. The determinant of the error matrix represents the overall variance of the fit. Because the standard deviation is the square root of the variance, the fit error F (in percent) evaluated to one standard deviation is given by[122]

$$F = (100\%)[\text{S.D.}/(\prod_{i=1}^{n} |A(i)|)]^{1/n} \quad , \tag{43}$$

where

S.D. = standard deviation of the fit,
n = number of parameters,
A(i) = parameter number "i."

This method of calculating fit error is a qualitative measure of the goodness of fit and is not absolute.[122] For a more detailed discussion of the error in the fit, see Draper and Smith,[128] Bevington,[110] and Roscoe and Furr.[122] A more detailed account of nonlinear least-squares fitting can be found in the original references listed above or in the books by Draper and Smith[128] and Bevington.[110]

In summary, the use of two-component tailing and fitting by the variable-metric method is preferred. However, if only a small computer is available, simpler analytical functions, using the random-search method of least-squares fitting to perform quantitative analysis, may be employed.

The results of any fitting routine should always be thoroughly inspected by a competent analyst. No program can consistently produce reliable results for a wide range of sample data; therefore, there is no substitute for the experienced spectroscopist.

5.1.4 Automatic Analysis

Most environmental laboratories adopt some form of automatic analysis of germanium spectra. The degree of automation is influenced by many factors, such as sample load, available equipment, available manpower, and budgets. Very few laboratories have automated their analyses to the same degree or in the same way.

Automated analysis can provide reduced costs for analyzing samples, improvements in analytical precision, improved methods of storing and handling data, and other related benefits. Reduction in costs for analyzing samples depends on actual sample load and is often less than would be expected because initial costs of equipment and system development are so high. The cost of training personnel to operate the system properly is also substantial. One great benefit of a highly automated system is the improvement in the analytical precision possible if the system is properly developed and used.

Sophisticated programs for automatic analysis of data can rapidly and accurately analyze germanium spectra that would be virtually impossible to analyze manually in an equivalent amount of time. Errors that occur frequently in manual analysis are virtually eliminated by computer processing. Data from a fully automated system of analysis can be output in a form that is readily adaptable to report preparation for regulatory agencies or other purposes. The data, depending on the system available, can also be transferred directly into a data bank, where it is stored for later use in reports covering long periods or for statistical examination and evaluation of the results of an environmental monitoring program.

Most programs for automatic analysis of germanium spectra can be separated into two parts, peak analysis and radionuclide identification.[27]

5.1.4.1 Peak Analysis

Peak analysis provides for input and reduction of the spectral data into energies and intensities for each FEP. This may require several program subdivisions, which will read in the data, smooth the data (Section 5.1.1), locate peaks (Section 5.1.2), determine the net counts in the FEPs (Section 5.1.3), determine the energies of the FEPs (Section 4.4.1), and determine the gamma emission rates for each FEP (Section 4.4.2).*

Transfer of spectral data to the analysis program is usually not a significant problem. If a large computer is being used for data analysis, the data may be entered by card or magnetic tape. For card entry, the format of data can be arranged as desired. Magnetic tape must be formatted as the program requires, or a separate program must transfer the data from the tape to the program, reformatting it in the process.

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*The gamma emission rate is calculated by using Equation (8): $N_\gamma = C/\varepsilon$ (Section 4.4.2.4.)

The use of an inhouse minicomputer for spectral analysis usually may be handled by directly interfacing the spectroscopy system to the computer and reading data under program control. If direct linkage is not possible, magnetic or paper tape may be used with the spectral data being read under program control by the computer. Usually, any process for transferring data is a simple one for a knowledgeable programmer.

The operations of peak analysis have been fully discussed in Sections 5.1.1 through 5.1.4. A program that performs all these analytical operations in the proper sequence is usually a quite sophisticated program, and considerable effort is often spent establishing routine operation of the program. Several such computer programs are available and widely used. These programs are referenced in this report in the particular section (5.1.1 through 5.1.4) in which the various features of spectral analysis were discussed.

5.1.4.2 Nuclide Identification

The stage of nuclide identification is often omitted from analysis programs.[86-88,94,123] Such programs provide information on only the energy and intensity of each FEP. Nuclide identification uses the energy and intensity of the FEP from the first stage of data analysis to deduce the component radionuclides, determine their activities, evaluate the error in the determined activities, and output the results in a particular format. Of course, such an identification package can be added to one program from another or written by the user to his own specifications.

The first item necessary for nuclide identification is a radionuclide library containing the most probable spectral components of the sample. Generally, a subroutine in the main program is used to initiate and to update this library.[27,29] Such a subroutine should produce a file that can be easily and efficiently searched by other subroutines used in the identification process. The file may typically contain data on (1) index position (a number indicating the numerical position of the entry in the file); (2) symbol of the element; (3) mass number; (4) energy and intensity of selected gamma rays emitted by the radionuclide; (5) half-life of the radionuclide; and (6) parent-daughter relationships of the particular radionuclide. The decay scheme information used in these libraries can be obtained from nuclear data sheets[45] or other compilations.[30,146]

Several different radionuclide libraries may be prepared and used for each specific type of sample. (For example, one library may be used for spectra containing mainly fission products, and another may be used for spectra containing mainly natural products.) Careful preparation and use of these libraries can greatly facilitate accurate identification and quantification. Each library should be prepared carefully, so that all probable components of the sample are included, but no extraneous components are present. This minimization of the library size can vastly speed up identification. Radionuclides can be added and deleted until optimum libraries are evolved for all sample types.

Most programs tentatively identify radionuclides on the basis of matching energies. In other words, any nuclide in the library that has a gamma-ray energy listed within a specified range of the FEP usually is selected as a possible candidate for that FEP. Those radionuclides that have half-lives that are short compared with the sample age can then be eliminated from consideration, because such radionuclides would have decayed to a nondetectable level after several (typically six to ten) half-lives.

The tests based on energy and half-life may be sufficient to identify the radionuclides within environmental samples with very few components, and these are the only tests that can be applied to radionuclides with only one abundant gamma ray. For radionuclides with more than one abundant gamma ray, a test that matches peaks in the unknown spectrum to possible radionuclides and evaluates the agreement between computed and reported energy values and intensity ratios for FEPs is often applied. A close match for energy and intensity between two or more gamma rays of an individual radionuclide usually is considered a positive identification except for very complex spectra.

When FEPs of the unknown spectrum have been assigned to the component radionuclides, the activities of these radionuclides can be calculated. Many programs simply calculate the activity A of a radionuclide using the observed gamma-ray emission rate N_γ from a single FEP:

$$A = N_\gamma/(P_\gamma f) , \tag{44}$$

where

P_γ = gamma-ray emission probability per decay (i.e., the branching fraction),
f = factor to convert counts to the desired activity unit (e.g., 3.7×10^4 disintegrations per second per microCurie).

This calculation fails to use a large amount of available data when a radionuclide emits two or more intense gamma rays. In such cases, the activity can be better estimated by calculating the final activity of the particular radionuclide by use of a weighted average of the observed emission rates from all FEPs belonging to the given radionuclide. Thus, the expression for the activity $\bar{A}$, based on a weighted-average calculation, would be given by

$$\bar{A} = (\sum_{i=1}^{n} A_i W_i)/\sum_{i=1}^{n} W_i , \tag{45}$$

where

n = total number of FEPs used in the weighted average,
Ai = activity calculated from equation based on the observed ratio of gamma emission of the "i"th FEP,
Wi = weighting factor for the "i"th FEP.

The weighting factors should be chosen so that[110]

$$W_i = 1/\sigma_i^2 \quad , \tag{46}$$

where

σ_i = total uncertainty in the activity if it were calculated from the "i"th FEP.

The uncertainty $\sigma_{\bar{A}}$ in the weighted-average activity is given by

$$\sigma_{\bar{A}}^2 = 1/\sum_{i=1}^{n} (1/\sigma_i^2) \quad , \tag{47}$$

where all terms are as previously defined.

The total uncertainty σ_i should combine both the uncertainty in the observed rate of gamma emission of the sample (i.e., the statistical uncertainty and uncertainties from the fitting process if a fitted technique was used) and the uncertainty in the probability of gamma-ray emission per decay. Often, the uncertainty in the probability of gamma-ray emission is not known, and this contribution to the total uncertainty is ignored.

The approach outlined above cannot account for unresolved interferences between peaks. This problem can be solved by forming a matrix of linear equations that describe the spectral intensity of each contributor to the FEP. Each peak is assumed to be made up of a linear combination of gamma rays from one or more components.[27,79,147] The intensity of the "i"th peak I_i is given by

$$I_i = \sum_{j=1}^{m} \varepsilon_i A_j P_{ij} \quad , \tag{48}$$

where

ε_i = detection efficiency for the "i"th FEP,

A_j = activity of the "j"th radionuclide,

P_{ij} = gamma-ray emission probability per decay for the "i"th line of the "j"th radionuclide.

Equations are written in matrix form for each FEP. Interdependent sets of equations are isolated and solved by the method of least-squares.[27]

The program GAMANAL, developed by Gunnink and Niday,[27] is applicable to a wide range of samples, some of which have very complex spectra. GAMANAL uses the most sophisticated methods for radionuclide identification and quantification described in the literature. The program incorporates a series of spectral tests that are used to determine the radionuclide composition of a sample. Each test assigns a confidence index to each candidate radionuclide. The most probable component radionuclides are chosen to reflect those with the highest final confidence index, which is simply the product of the confidence-level indices from each individual test. A matrix of linear equations is set up and solved by the method of least-squares.

Several other computer programs for automatic radionuclide identification have been developed for routine use.[27,78,79,122,147-153] Some of these programs are simply modifications or adaptations of other existing software, whereas others contain entirely new approaches to the problems of radionuclide identification.

The size and type of computer available for analysis of germanium spectra greatly influence the method of analysis selected by the user. Several programs are written in modular form so that they can be adapted to either a small computer or a sophisticated, programmable calculator.

One approach to providing automatic analysis of germanium spectra followed in many laboratories is to develop programs for each specific task. As the work load increases or as the need for more sophisticated or accurate methods increases, software is deleted from or added to the existing program structure.

Many laboratories are purchasing germanium spectroscopy systems that provide a combination of data acquisition and data reduction capabilities. Many of these systems offer the advantage of automatic quantification and identification of radionuclides without the necessity of the user developing his own software. Also, the manufacturers often offer complete software support, including updates and new features. Many systems use the principle of multiple core overlay to allow a sophisticated program to be executed with a relatively small computer; however, before such a system is purchased, the software to be supplied by the vendor should be carefully evaluated to ensure that it will adequately meet the needs of the laboratory. In summary, several points should be considered when the question of germanium spectrum analysis is addressed:

1. Because no fully automatic system exists that can produce accurate, reliable results without fail, all results must be carefully reviewed by a competent analyst.

2. Although the selection of an analytical methodology should be a thorough process based partly on current sample load and costs, a system should be chosen which will meet the needs of the laboratory for several years. This selection process must consider that the initial cost of setting up the system is a major expense, not to be repeated frequently.

3. The technical knowledge and time required to obtain reliable results should not be underestimated.

4. If a large computer is used, the cost for processing the spectra should be considered. There may be a minimum charge for each computer run so that the cost for processing a single spectrum would be quite high; however, if many spectra are processed in each run, the cost per spectra would decrease.

5.2 LOWER LIMIT OF DETECTION

Detection limits are used to measure the detection capability of a given measurement process. These limits are determined from considerations of the procedures and equipment used in a specific analytical technique. For radioanalytical analyses, the detection limits are becoming increasingly important, because they are often the criteria used by many regulatory agencies to define minimum acceptable performance for an analytical procedure.

The confusion over proper mathematical definitions of the many terms used to define detection limits has been noted by Currie.[154] The implied statistical significance of these terms has also been a source of confusion. To avoid any confusion in this discussion, we will adopt the definition of the detection limit, the lower limit of detection (LLD), given by Harley[17]:

> The smallest amount of sample activity, using a given measurement process (i.e., chemical procedure and detector) that will yield a net count for which there is confidence at a predetermined level that activity is present.

This particular definition was chosen because of its clear statistical meaning and its use by other laboratories and regulatory agencies. The LLD may be approximated as

$$\mathrm{LLD} \cong (K_\alpha + K_\beta) S_o \gamma \ , \tag{49}$$

where

K_α = value of the upper percentile of the standardized normal variate corresponding to the preselected risk of a type I error (i.e., concluding that activity is present when in fact activity is not present),
K_β = value of the upper percentile of the standardized normal variate corresponding to the preselected risk of a type II error (i.e., concluding that activity is not present when in fact it is present),
S_o = established standard error for the net counting rate of the sample,
γ = factor used to convert count rate due to a given radionuclide to activity.

If the probability for the type I error is set at the same level as that for the type II error, if the counting times for background and the sample are equal, and if the gross activity and the background are approximately equal, the equation can be written more simply as

$$\mathrm{LLD} \cong 2K_1 \sqrt{2S_b}\, \gamma \ , \tag{50}$$

where

$K = K_\alpha = K_\beta$,
S_b = background counting rate.

The probabilities of the type I and type II errors are usually chosen to be 5 percent each. Therefore, two relationships result:

$$2K\sqrt{2} = 4.66 \,, \tag{51}$$

and

$$\mathrm{LLD} = 4.66\sqrt{S_b}\,\gamma \tag{52}$$

Although the 5 percent probability level has been widely used, there is no reason why other probability levels could not be chosen to establish a particular confidence level. Also, the importance of type I or type II error can be individually determined. Values of the $2K\sqrt{2}$ term for other probability levels are given in the HASL laboratory manual.[17] Other less common values of K_α and K_β can be found in most statistics books.

In the discussion of LLD above, the variability in other parameters, such as detection efficiency and obtaining representative samples, is neglected, although their relative errors may be comparable to the variability in the count rates. These other sources of error have been addressed by Johnston[155] and Bowman and Swindle.[156]

The value of reducing the variability in the counting procedure and the chemical procedure depends on the precision of the system for sample measurement.[157] Low values for LLDs and low variabilities in the chemical and counting procedures are not of value if the variability in the sampling procedure is large.

Methods of reporting results consistent with the HASL definition of LLD are given by Currie,[154] Hartwell,[158] and Lochamy.[159]

Regulatory agencies are beginning to specify the LLD that must be met for a particular type of analytical result. In specifying these requirements, the level of confidence and the value of the $2K\sqrt{2}$ term also are being outlined. To attain a given LLD, all terms used to calculate the LLD must be considered. One term, γ, is given by

$$\gamma = 1/(RVEfDA\sqrt{t}) \,, \tag{53}$$

where

R = chemical yield or recovery for all steps within the procedure,
V = volume or mass of sample which is used for the analysis,
E = absolute counting efficiency of the detector for the FEP,
f = number of photons of a given energy emitted per nuclear decay (i.e., the branching fraction),
D = radioactive decay fraction,
A = unit conversion factor (e.g., 2.22 pCi/dpm),
t = length of the counting interval.

The radioactive decay factor, which accounts for the decay from the time of sample collection to the time the sample is counted, is given by

$$D = \exp[-0.693(t_i - t_s)/t_{1/2}] , \qquad (54)$$

where

t_i = time at the midpoint of the counting interval,
t_s = time of sample collection,
$t_{1/2}$ = half-life of the radionuclide.

The value of the terms R and V are affected by the procedure chosen. The value of the D term is affected strictly by the promptness with which a sample is analyzed. This interval should be kept to a minimum so that radionuclides with short half-lives can be determined accurately; time, obviously, is not critical for radionuclides with long half-lives. The counting efficiency and counting rate of the background are determined by the equipment available.

The combination of procedure and equipment that can yield an acceptable LLD cannot be straightforwardly determined. In practice, assembly and testing of several trial combinations of equipment and procedures experimentally may be necessary before an acceptable performance is achieved.

When more than one radionuclide is present in a sample, the interfering radionuclides will effectively increase the background over large regions of the gamma spectrum. Therefore, the LLD calculated for a particular gamma-emitting radionuclide will vary with the concentration of other radionuclides present in the sample, and because the concentration of other gamma-emitting radionuclides within the sample are unknown before analysis, a valid LLD for a given sample cannot be calculated before analysis.

For comparative purposes only, one can calculate a nominal LLD for a given radionuclide. However, all conditions under which these LLDs are determined must be stated so that valid comparisons can be made with other available data. Tables 9 through 13 list some nominal values for the LLDs of various radionuclides in several counting geometries. These LLDs have been calculated under the assumptions that no chemical separation or concentration is performed on the sample and that the time between sample collection and counting is one week. The counting rate of the background was determined by counting blank samples in identical geometries. The blank samples are described in Table 14, and the detectors and shields used in this determination are described in Table 1.

The counting rate of the background, S_b, for detector 1 was estimated by summing over a region corresponding to 5 keV for FEPs with energies less than 400 keV and over 6 keV for FEPs with energies greater than 400 keV. The counting rates of the background for detectors 2 and 3 were estimated by summing over a region corresponding to 3 keV for FEPs with energies less than 400 keV and over 3.5 keV for FEPs with energies

TABLE 9. LLD VALUES (pCi/L) FOR 3.5-L GEOMETRY USED FOR WATER[a]

Nuclide	Energy (keV)	LLD values by detector		
		Detector 1	Detector 2	Detector 3
^{144}Ce	133.5	24	12	15
^{51}Cr	320.1	32	15	19
^{131}I	364.5	5.8	2.9	3.5
^{106}Ru	511.8	20	14	16
	622.1	29	15	17
^{140}Ba-La[b]	537.4	18.0	9.2	10
	1596.2	4.7	2.3	2.8
^{134}Cs	604.7	3.0	1.4	1.7
	795.8	3.8	1.8	2.0
	569.3	19	9.4	11
^{137}Cs	661.6	3.4	1.7	2.1
^{95}Zr-Nb	756.0	5.7	2.7	3.3
	724.0	6.9	3.3	4.0
	765.0	3.1	1.5	1.7
^{58}Co	810.6	3.1	1.6	1.8
^{54}Mn	834.8	3.0	1.7	1.8
^{65}Zn	1115.5	6.1	3.2	3.6
^{60}Co	1173.2	3.1	1.8	2.0
	1332.5	3.0	1.7	1.9

[a] Considering the variability in the branching fractions, the counting rate of background, and the efficiency of detection, the overall variability in the values assigned as LLD is about 10 percent. All LLDs are calculated for a counting time of 54,000 s (15 h).

[b] For the purposes of calculating the LLD values, ^{140}Ba (half-life, 12.8 d) and its daughter ^{140}La (half-life, 40.2 h) are assumed to be in equilibrium.

TABLE 10. LLD VALUES (pCi/g) FOR 0.5-L GEOMETRY USED FOR WATER[a]

Nuclide	Energy (keV)	LLD values by detector		
		Detector 1	Detector 2	Detector 3
^{144}Ce	133.5	60	27	28
^{51}Cr	320.1	92	44	37
^{131}I	364.5	17	7.9	7.3
^{106}Ru	511.8	65	35	40
	622.1	98	40	37
^{140}Ba-La[b]	537.4	59	38	23
	1596.2	16	7.2	7.0
^{134}Cs	604.7	9.9	4.4	3.9
	795.8	12	5.2	4.6
	569.3	58	28	25
^{137}Cs	661.6	11	4.9	4.8
^{95}Zr-Nb	756.0	18	8.0	8.0
	724.0	22	10	8.8
	765.0	9.3	4.7	4.1
^{58}Co	810.6	9.9	4.6	4.2
^{54}Mn	834.8	10	4.6	4.3
^{65}Zn	1115.5	9.3	9.9	7.8
^{60}Co	1173.2	11	4.9	4.4
	1332.5	11	4.8	5.0

[a] Considering the variability in the branching fractions, the counting rate of background, and the efficiency of detection, the overall variability in the values assigned as LLD is about 10 percent. All LLDs are calculated for a counting time of 54,000 s (15 h).

[b] For the purposes of calculating the LLD values, ^{140}Ba (half-life, 12.8 d) and its daughter ^{140}La (half-life, 40.2 h) are assumed to be in equilibrium.

TABLE 11. LLD VALUES (pCi/g) FOR GEOMETRY USED FOR VEGETATION[a]

Nuclide	Energy (keV)	LLD values by detector		
		Detector 1	Detector 2	Detector 3
^{144}Ce	133.5	0.16	0.090	0.090
^{51}Cr	320.1	0.34	0.14	0.13
^{131}I	364.5	0.067	0.026	0.026
^{106}Ru	511.8	0.23	0.15	0.14
	622.1	0.37	0.15	0.15
^{140}Ba-La[b]	537.4	0.25	0.085	0.085
	1596.2	0.061	0.028	0.028
^{134}Cs	604.7	0.039	0.015	0.016
	795.8	0.046	0.019	0.018
	569.3	0.24	0.091	0.095
^{137}Cs	661.6	0.045	0.017	0.019
^{95}Zr-Nb	756.0	0.071	0.028	0.030
	724.0	0.083	0.034	0.034
	765.0	0.039	0.015	0.016
^{58}Co	810.6	0.039	0.016	0.016
^{54}Mn	834.8	0.038	0.015	0.017
^{65}Zn	1115.5	0.080	0.034	0.033
^{60}Co	1173.2	0.041	0.018	0.018
	1332.5	0.043	0.019	0.019

[a] Considering the variability in the branching fractions, the counting rate of background, and the efficiency of detection, the overall variability in the values assigned as LLD is about 10 percent. All LLDs are calculated for a counting time of 54,000 s (15 h).

[b] For the purposes of calculating the LLD values, ^{140}Ba (half-life, 12.8 d) and its daughter ^{140}La (half-life, 40.2 h) are assumed to be in equilibrium.

TABLE 12. LLD VALUES (pCi/g) FOR GEOMETRY USED FOR SOIL[a]

Nuclide	Energy (keV)	LLD values by detector		
		Detector 1	Detector 2	Detector 3
^{144}Ce	133.5	0.042	0.027	0.022
^{51}Cr	320.1	0.072	0.042	0.032
^{131}I	364.5	0.013	0.0070	0.0070
^{106}Ru	511.8	0.049	0.038	0.037
	622.1	0.081	0.038	0.036
^{140}Ba-La[b]	537.4	0.053	0.023	0.019
	1596.2	0.014	0.0058	0.0069
^{134}Cs	604.7	0.0087	0.0040	0.0031
	795.8	0.010	0.0050	0.0039
	569.3	0.055	0.0260	0.022
^{137}Cs	661.6	0.011	0.0047	0.0039
^{95}Zr-Nb	756.0	0.017	0.0078	0.0062
	724.0	0.019	0.0093	0.0078
	765.0	0.0087	0.0039	0.0039
^{58}Co	810.6	0.0087	0.0047	0.0031
^{54}Mn	834.8	0.0087	0.0047	0.0039
^{65}Zn	1115.5	0.018	0.0086	0.0078
^{60}Co	1173.2	0.0087	0.0047	0.0039
	1332.5	0.0093	0.0039	0.0039

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[a] Considering the variability in the branching fractions, the counting rate of background, and the efficiency of detection, the overall variability in the values assigned as LLD is about 10 percent. All LLDs are calculated for a counting time of 54,000 s (15 h).

[b] For the purposes of calculating the LLD values, ^{140}Ba (half-life, 12.8 d) and its daughter ^{140}La (half-life, 40.2 h) are assumed to be in equilibrium.

TABLE 13. LLD VALUES (pCi/L) FOR GEOMETRY USED FOR AIR FILTERS[a]

Nuclide	Energy (keV)	LLD values by detector		
		Detector 1	Detector 2	Detector 3
^{144}Ce	133.5	10.8	3.2	3.4
^{51}Cr	320.1	15.0	6.2	7.0
^{131}I	364.5	2.8	1.1	1.4
^{106}Ru	511.8	11.0	6.5	5.8
	622.1	17.0	7.3	7.4
^{140}Ba-La[b]	537.4	9.8	3.9	4.1
	1596.2	3.2	1.3	1.3
^{134}Cs	604.7	1.6	0.76	0.95
	795.8	2.1	0.92	0.91
	569.3	11.0	3.8	4.7
^{137}Cs	661.6	1.9	0.85	0.88
^{95}Zr-Nb	756.0	3.0	1.3	1.4
	724.0	4.0	1.6	1.8
	765.0	1.8	0.69	0.78
^{58}Co	810.6	1.9	0.78	0.70
^{54}Mn	834.8	1.7	0.83	0.81
^{65}Zn	1115.5	3.6	1.5	1.9
^{60}Co	1173.2	1.9	0.89	0.99
	1332.5	2.0	0.89	0.86

[a] Considering the variability in the branching fractions, the counting rate of background, and the efficiency of detection, the overall variability in the values assigned as LLD is about 10 percent. All LLDs are calculated for a counting time of 54,000 s (15 h).

[b] For the purposes of calculating the LLD values, ^{140}Ba (half-life, 12.8 d) and its daughter ^{140}La (half-life, 40.2 h) are assumed to be in equilibrium.

TABLE 14. PREPARATION OF BACKGROUND STANDARDS FOR DETERMINATION OF LLD

Geometry	Description
3.5-L for water	Clean, unused Marinelli beakers (3.7-L total volume) were filled with 3.5 L of distilled H_2O. The water was aerated in the Marinelli beaker for about 2 h with inert N_2 gas to reduce radon content of the distilled H_2O. A layer of plastic film was placed over the mouth of the beaker, and the beaker lid was installed. The plastic film and lid were sealed to the beaker with masking tape.
0.5-L for water	0.6-L Marinelli beakers were prepared in a manner similar to that described above with 0.5 L of distilled, aerated H_2O.
Soil	600 g of analytical grade salt (NaCl) was weighed and placed into an unused 0.5-L Marinelli beaker. The lid of the container was sealed to the sample container with masking tape.
Vegetation	An unused 0.5-L Marinelli beaker was filled with ground styrofoam chips. Analytical grade NaCl was added until the final weight was achieved; the container lid was then sealed in place with masking tape.
Air filter	A 5-cm-diameter, plastic petri dish with an air filter inside was sealed closed with adhesive tape.

greater than 400 keV. The widths of these regions were selected to optimize the factor $\sqrt{S_b}/\varepsilon$, where ε is the absolute efficiency of detection of the FEP.

The LLD values that are applicable to a given analytical result depend on the methods used to analyze the data. For example, if a peak-search routine should be unable to detect FEPs at the calculated LLD level, the LLD would not apply to the results obtained using that peak-search routine.

Another question is whether a background estimate should come from the extrapolation of counts on either side of the peak or from summing the photopeak area of a well-known background. Spectra from samples containing LLD-level spikes were compared with those from 84 background runs. Tests showed a significant difference at the 95 percent confidence level in areas where no activity was expected to be present. This clearly indicates that the background should be determined from the same spectrum that is being analyzed.

SECTION 6

COMPARISON OF GERMANIUM AND NaI(Tℓ) SYSTEMS FOR GAMMA SPECTROSCOPY

6.1 SYSTEM SENSITIVITIES

Two principal gamma-ray detection systems are used to analyze environmental samples: germanium detectors and thallium-activated sodium iodide [NaI(Tℓ)] detectors. In recent years discussion has arisen regarding the superiority of germanium vs. NaI(Tℓ) systems for routine analysis of gamma rays from low-activity samples: Which system yields the greatest amount of usable data in the most cost-effective manner? For applications of these systems to environmental analysis, this question can be approached with regard to LLD, cost, and ability of the system to produce quality data in a reasonable length of time.

Some common characteristics of germanium [Ge(Li) and HPGe] and NaI(Tℓ) detector systems are presented in Table 15. Germanium systems are characterized by high cost, excellent resolution, and low detection efficiency, whereas NaI(Tℓ) systems have relatively poor resolution, high detection efficiency, and possibly lower cost.

Specific comparisons of germanium and NaI(Tℓ) systems are complicated by differences in analytical methods used in spectral analysis. For example, one of the most common methods for NaI(Tℓ) spectral analysis is the least-squares method used in computer codes such as ALPHA-M.[10,160-162] Analytical systems for spectra produced by germanium-based systems generally use the fitting of a Gaussian or other higher-order function to the spectral data (Section 5.1).

Methods for determining background also differ for various analytical techniques, and consequently, comparisons of calculated LLD values for systems using these different analytical methods must be generic in nature. Erroneous conclusions can be drawn if LLDs calculated for specific analytical techniques are applied empirically.

Table 16 is a compilation of LLD values for spectra containing a single radionuclide (single-nuclide LLDs) calculated by the HASL-300 method for several germanium and NaI(Tℓ) systems.[158] Background for the germanium detectors was estimated by evaluating the background in spectral regions corresponding to an FEP with the use of procedures outlined in Table 9 and Section 5.2. The LLD values for NaI(Tℓ) detectors were estimated from the output of the ALPHA-M program[18,163,164] for data entitled "least-squares" or were calculated by means of hand-determined estimates of background and efficiency for the data entitled "FEP." These comparisons are of actual environmental geometries rather than of the ideal point-source configurations usually cited when such comparisons are made.[165]

Data in Table 16 indicate that the detection system with the lowest calculated LLD varies with radionuclide and gamma-ray energy. Although germanium detectors have an inherently lower total detection efficiency than do NaI(Tℓ) detectors, LLD values for germanium detectors are not

TABLE 15. CHARACTERISTICS OF GERMANIUM AND NaI(Tℓ) SYSTEMS FOR GAMMA-RAY SPECTROSCOPY

Item	Germanium	NaI(Tℓ)
Equipment	Detector, cryostat, FET preamplifier, linear amplifier, high-voltage power supply, ADC, MCA (computer or hardware)	Detector, photomultiplier, preamplifier, linear amplifier, high-voltage power supply, ADC, MCA, computer
Characteristics of the detector		
Resolution	≃2keV	≃55keV
Efficiency[a]	1-30%	
Operating temperature	-200°C	20°C
Detector material	Diode fabricated from HPGe ingot or Ge(Li) ingot	Sodium iodide with thallium as impurity
Capital cost		
Detector	$5,000-$30,000	$1,000-$2,000
Electronics[b]	$4,000	≃$3,000
MCA	$10,000-$100,000	$10,000
Peripherals (disks, tapes, printers, etc.)[c]	$2,000-$15,000	$2,000-$25,000
Total equipment cost	$27,000-$132,000	$16,000-$40,000
Operating cost (per year)		
Computer cost	$0-$5,000	$5,000
Liquid nitrogen	≃$800	-

[a] Efficiency compared with a 76- by 76-mm NaI(Tℓ) crystal, source-to-detector distance of 25 cm.

[b] Assuming one ADC per detector.

[c] May be included in capital cost if a computer-based MCA is purchased.

TABLE 16. LLD VALUES (pCi/L) FOR 3.5-L GEOMETRY FOR SAMPLES CONTAINING A SINGLE RADIONUCLIDE

		LLD values by detector[a]				
Nuclide	Energy (keV)	Germanium detector 1	Germanium detector 2	Germanium detector 3	10- by 10-cm NaI(Tℓ) least-squares	10- by 10-cm NaI(Tℓ) FEP
^{144}Ce	133.5	88.2	44.1	55.1	28.7	46.2
^{51}Cr	320.1	118.0	47.8	58.8	49.7	45.8
^{131}Ru	364.5	25.7	5.88	6.98	6.13	9.97
^{106}Ru	511.8	73.5	51.4	58.8	28.3	43.9
	622.1	107.0	55.1	62.5	-	99.25
^{140}Ba	537.4	73.5	23.2	25.4	6.54	33.3
	1596.2	19.5	5.88	6.98	-	87.3
^{134}Cs	604.7	11.0	5.14	6.25	6.31	8.31
	795.8	14.0	6.61	7.35	-	-
	569.3	69.8	34.5	40.4	-	10.3
^{137}Cs	661.6	12.5	6.25	7.72	6.88	10.2
^{95}Zr-Nb	756.0	20.9	9.92	12.1	6.77	-
	724.0	25.4	12.1	14.7	-	-
	765.0	11.4	5.51	6.25	-	9.85
^{58}Co	810.6	11.4	5.88	6.61	6.88	10.18
^{54}Mn	834.8	11.4	5.25	6.61	6.21	10.24
^{65}Zn	1115.5	22.4	11.8	13.2	13.9	21.9
^{60}Co	1173.2	11.4	6.61	7.35	6.02	10.0
	1332.5	11.0	6.25	6.98	-	9.26

[a] Counting time of 4,000 s.

correspondingly higher. Low LLD values for germanium-based systems result from low background of the crystal over the regions used to calculate the LLDs. These LLD values are system-specific and not generally applicable.

Comparison of LLD values is further complicated when LLD values for samples containing more than one radionuclide (multinuclide LLDs) are considered. In Table 17 two cases are presented which show the variation in LLD observed for multinuclide samples counted on germanium and NaI(Tℓ) systems. One can see that the germanium LLD values for ^{137}Cs and ^{60}Co (about 20 pCi/L) in a 3.5-L Marinelli geometry were affected to a greater extent when compared with the single-nuclide case, than those projected by the NaI(Tℓ) least-squares techniques. A conflicting case is found, however, when ^{54}Mn and ^{58}Co are prepared in the 3.5-L Marinelli geometry at about 20 pCi/L. The LLD values for these nuclides undergo a more substantial increase for the NaI(Tℓ) least-squares technique than for the germanium system.

This apparent discrepancy results from the analytical technique for the two types of data. The least-squares technique for NaI(Tℓ) uses standard spectra for each nuclide and the background in the fitting procedure. The entire sample spectrum is evaluated rather than just the photopeak area. The resultant LLD values for a particular nuclide in a particular sample are produced from diagonal elements of the inverse matrix.[10,166] The LLD values increase rapidly for the least-squares technique as concentration increases, but not as rapidly as they would if simple FEP analysis, as used for the germanium data, were used.

However, the case of ^{58}Co and ^{54}Mn illustrates the weak point of least-squares analysis. These nuclides have essentially the same gamma-ray spectrum and, as indicated in Table 17, are so close in energy that the NaI(Tℓ) detector cannot resolve them. If the two nuclides had other strong, distinguishing gamma-ray emissions, this analysis would be less difficult; however, as it is, the resultant LLD values inflate rapidly as a result of the interference.[10] On the other hand, the resolution of the germanium detector allows the simple FEP fit to produce significantly lower LLD values.

As noted in Section 5.2, the ultimate lower limit of detection depends on the entire spectroscopy system--the detector, the counting system, and the analytical technique used to reduce data. The LLD value generated for the NaI(Tℓ) system is, in fact, a measure of the LLD of the system for that particular sample, background, and detector. The LLD values quoted for the germanium system may or may not be routinely achievable, depending primarily on the utility and accuracy of peak-locating and peak-fitting programs used for spectral analyses. Typically, with the relatively simple software for peak analysis supplied with many minicomputer-based germanium systems, counting times of several times those used for NaI(Tℓ) systems are required to achieve realistically comparable LLDs.

TABLE 17. LLD VALUES (pCi/L) FOR SAMPLES CONTAINING MORE THAN ONE RADIONUCLIDE

	LLD values by detector			
Energy (kev)	Multinuclide germanium detector 3	Single-nuclide germanium detector 3	Single-nuclide NaI(Tℓ) detector	Multinuclide NaI(Tℓ) detector
20 pCi/L of ^{137}Cs and ^{60}Co added to a 3.5-L Marinelli beaker				
661.62	17.5	7.72	6.88	9.14
1173.23	13.3	7.35	6.02	7.38
1332.52	12.4	6.98		
20 pCi/L of ^{54}Mn and ^{58}Co added to a 3.5-L Marinelli beaker				
810.6	12.9	6.61	6.88	18.2
834.8	12.3	6.61	6.21	14.7

6.2 SYSTEM COSTS

The cost of germanium and NaI(Tℓ) systems are determined by initial capital expenses and the costs of routine operation. The cost of germanium detectors, disregarding electronics and analytical systems, varies with the size and type of detector. Germanium detectors suitable for environmental analyses may range in cost from about $6000 for a small-volume, coaxial Ge(Li) (about 9 percent) detector to more than $30,000 for a large-volume Ge(Li) or HPGe detector. The typical cost for a 15 percent Ge(Li) detector is about $12,000, whereas NaI(Tℓ) detectors and associated photomultipliers range in cost from $1000 to $2000. The cost of supportive signal-processing electronics is about 50 percent greater for germanium systems than for NaI(Tℓ) systems. This increased cost results from a need for lower noise and greater electronic stability in processing output pulses from germanium detectors. The ADC cost can be considered equal for both spectroscopy systems; however, for a single detector, an ADC conversion gain of 4096 channels or greater is required to realize the superior resolution of a germanium detector fully. The NaI(Tℓ) detector can be used effectively with an ADC conversion gain of 256 channels. A signal mixer-router (SMR) may be used with an NaI(Tℓ) system, allowing more than one NaI(Tℓ) detector to be used with a single ADC. Similarly, several NaI(Tℓ) detectors can be used with a single MCA using the SMR-ADC-MCA system.

A need for several germanium detectors will require several MCA systems or a computer-based MCA with 20K (assuming 16-bit words) or more words of memory. For practical applications for which there are high sample loads and several germanium detectors, the computer-based MCA system combines a large analyzer memory with capabilities for reduction and analysis of data. Under these conditions, the computer-based MCA appears to be the most cost-effective system for acquisition and analysis of data for routine analysis using germanium detectors.

Analysis of a large number of NaI(Tℓ)-generated spectra by the least-squares technique also demands the use of a computer. Inherent in the cost of any NaI(Tℓ) system that uses spectral analysis by computer is the cost of transferring the data to the computer. This transfer can be accomplished by using microprocessors, magnetic tape, disk, teletype, or card punch. The cost of transfer, by either system peripherals or manpower, must be reflected in the cost of the system. The cost of the peripheral systems for NaI(Tℓ) spectroscopy might range from about $2000 to $25,000, depending on the sophistication and capabilities desired. A typical least-squares analysis of an environmental sample requires slightly more than one second of central processor time on a large computing machine. For a typical time-sharing system, this equates to about 25¢ per analysis, neglecting overhead expenses.

Another cost that must be considered for both NaI(Tℓ) and germanium systems that analyze data by computer is the cost of analyst time for review and validation of results from the computer analysis. Depending on the sophistication of the program used, this cost may or may not be negligible. Because no program for analysis of gamma-ray spectra, regardless of its complexity, is able to handle all data equally well, elimination of this cost for review seems unlikely. Experience with a small, microprocessor-based MCA system for germanium detectors has shown that up to one hour of analyst time can be required to ensure an accurate spectral analysis on a complex or low-level spectrum. However, this amount of time should not be required with the use of a more sophisticated analysis program. Results from least-squares analysis of NaI(Tℓ) spectra are generally reliable. Most of the analyst's time is spent ensuring that conditions are not present that could invalidate the analytical results produced by the program; for instance, the presence of a nuclide in the sample spectrum not accounted for by the standards in the program library could invalidate the results.

Many factors contribute to the cost (time) required for a system to produce quality data. Some of these factors, such as reliability of spectral analysis by computer, have already been mentioned. Other factors such as ease of calibration, stability of the system, and ease of setting up the system contribute to the overall functioning of the spectroscopy system. In this regard, germanium and NaI(Tℓ) systems have characteristic differences affecting their routine use.

Set-up of the system should be carefully considered when choosing a system for gamma-ray spectroscopy. Implementation of programs, such as ALPHA-M, for analysis of NaI(Tℓ) spectra, is time-consuming and demands a good working knowledge of computers and programming. Similarly, computer-based systems using germanium detectors require some knowledge of computer operation and programming for efficient use.

Calibration of the system cannot be separated from set-up of the system because information on calibration is required before one can begin analyses of sample spectra by computer. Systems based on germanium detectors are fairly easily calibrated for energy and efficiency response by measuring multinuclide, radioactive standard solutions in those geometries to be used for sample analysis. Calibration of counting efficiency can be based on detection efficiency for the FEP (Section 4.4.2). Energy calibration of a germanium system is easier than calibration of an NaI(Tℓ) system because of inherently better gain stability and linearity of the electronics used. Because the location of a peak can be determined with great accuracy in a germanium spectrum, an NBS-certified, multiline radioactive source is sufficient for routine energy calibration of germanium systems.

Calibration of NaI(Tℓ) systems can be much more tedious. For least-squares analysis, a standard containing the nuclide of interest of known activity must be counted in each sample geometry for each nuclide to establish a program library of reference spectra. If one considers a library of only twenty nuclides and five counting geometries, 100 radioactive standards must be prepared, counted, and evaluated to build the standard libraries for the least-squares program. Daily energy calibration [NaI(Tℓ)] is performed with a multiline standard such as ^{207}Bi.[9] Variations in system gain must be minimized from run to run; therefore, a spectral line such as that from ^{137}Cs (661.6 keV) must be correctly positioned between each analysis.[10] Most least-squares programs, such as ALPHA-M, can then make minor gain adjustments between the spectra in the standard library and an actual sample spectrum. The relative simplicity of calibrating germanium detectors allows flexibility in choosing and changing counting geometries quickly that is not afforded by the NaI(Tℓ) system.

6.3 SYSTEM APPLICABILITY

A measure of the overall accuracy of NaI(Tℓ) and germanium systems can be determined by comparing results for identical samples. Yule[162] presents comparative data on the quantitative and qualitative analyses of environmental standards for a germanium system using a TPA method to determine FEP intensity and for a 76- by 76-mm NaI(Tℓ) detector system using ALPHA-M for spectral analysis. Yule[162] and Wrenn et al.[167] conclude that, for a variety of sample types, the combination of NaI(Tℓ) detector and least-squares analysis can yield accuracy similar to that provided by analysis by germanium systems for shorter counting times than required for germanium analysis.

In Table 18 data are presented for the analytical results from an NaI(Tℓ) system using ALPHA-M analysis for EPA cross-check samples of gamma emitters in water. Each sample was counted in a 3.5-L Marinelli geometry. The counting time was 4000 s for the NaI(Tℓ) system and 14,400 to 54,000 s for the germanium system. As the data indicate, the two systems generally agree for quantitative assessment of identified nuclides. Our experience has indicated that less sophisticated programs of spectral analysis often used on minicomputers require longer counting times for accurate determinations of low-level activity than do NaI(Tℓ) least-squares analyses. Other more sophisticated spectral programs may be able to perform these analyses accurately with shorter counting times.

Table 19 presents some advantages and disadvantages of germanium and NaI(Tℓ) systems. Although each detector system has characteristics that are desirable for environmental analyses, neither detector system encompasses all the necessary characteristics to enable optimum analysis of all sample types. A logical approach to environmental analyses seems to include a program for gamma spectrometry that uses both germanium and NaI(Tℓ) detectors. Each detector should be used for those sample types for which it can perform the most complete, accurate, and rapid analyses. For example, NaI(Tℓ) systems appear to be particularly suited to the analysis of routine samples that normally contain a known set of radionuclides. If abnormally high activity is detected in the sample by least-squares analysis or if review of the results of the least-squares analysis indicates the presence of unknown nuclides or an inaccurate determination of the concentration of routine nuclides, the sample could subsequently be counted on a germanium detector for more detailed analysis. Germanium detectors appear to be well suited for analysis of samples whose spectra are known to be complex or not routine in nature, such as soil, uranium mill tailings, or effluents from nuclear power plants.

TABLE 18. CROSS-CHECK RESULTS (pCi/L) FOR GAMMA EMITTERS IN WATER

Nuclide	Activity reported by EPA[a]	NaI(Tℓ)-ALPHA-M (4000 s)	Ge(Li) (54000 s)
		December 1976	
^{51}Cr	104±15	97±40	146±32
^{60}Co	0±15	3±4	0±0
^{65}Zn	102±15	100±10	110±6
^{106}Ru	99±15	83±19	101±15
^{134}Cs	93±15	101±6	81±3
^{137}Cs	101±15	104±6	97±3
		February 1977[b]	
^{51}Cr	202±30	193±41	171±55
^{60}Co	45±15	47±4	47±9
^{65}Zn	37±15	38±9	50±15
^{106}Ru	151±23	140±20	141±48
^{134}Cs	76±15	78±6	72±9
^{137}Cs	39±15	39±5	41±8
		April 1977	
^{51}Cr	177±27	144±38	168±28
^{60}Co	35±15	36±3	33±4
^{65}Zn	50±15	52±9	50±8
^{106}Ru	72±15	65±16	66±24
^{134}Cs	27±15	24±4	23±4
^{137}Cs	21±15	22±4	19±2

[a] Error limits at the 99 percent confidence level.

[b] February Ge(Li) results are based on a 14,400-s counting time.

TABLE 19. ADVANTAGES AND DISADVANTAGES OF GERMANIUM AND NaI(Tℓ) SPECTROMETRY SYSTEMS FOR GAMMA-RAY SPECTROSCOPY

Advantages of germanium systems

Superior resolution; ~1.6 keV for 661.6-keV (^{137}Cs) gamma ray resulting in accurate determination of the energy of FEPs.

Ease of calibration and standardization; new or old geometries may be determined at short notice.

Lack of appreciable problems with gain shift.

Most components of a gamma-ray spectrum can be identified by sight.

Nuclide libraries on the computer can be easily revised and expanded without additional calibration.

Components of a spectrum not identified by computer can still be identified by hand calculations.

Background can be estimated from the baseline around the FEP.

Disadvantages of germanium systems

Cost is high.

Small volume and low efficiency of detection.

Large memory required for the MCA.

Reduction of data by computer necessary for complex or low-level analysis. Many software packages are unable to quantify nuclides of low activity accurately. Successful operation also requires personnel to have some knowledge of computers and programming.

Liquid nitrogen temperatures are required for the operation of both Ge(Li) and HPGe detectors.

Long counting times.

TABLE 19. (continued)

Advantages of NaI(Tℓ) systems

Large detector volume and high counting efficiency.

Short counting times required for sample analysis with least-squares techniques, compared with most germanium systems.

Detectors are low in cost.

Operation at room temperature.

Minimal memory required in the MCA.

Estimates of nuclide activity are based on the entire spectrum, not just a single measurement of the FEP.

Disadvantages of NaI(Tℓ) systems

Poor resolution; typically, 55 keV for 661.6-keV (^{137}Cs) gamma-ray.

Gain shifts with time and temperature.

Complex procedures for calibration and standardization.

Complex spectra require computer analysis. This requires access to a computer and personnel knowledgeable in computers and programming.

System is extremely sensitive to background fluctuations (primarily from ^{222}Rn and daughters).

Difficulty in separating overlapping or interfering single gamma rays.

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APPENDIX A

GERMANIUM DETECTOR LEAKAGE CURRENT TEST

Determination of the detector leakage current is a useful periodic maintenance check that can be performed by either maintenance personnel or the analyst. This check, which is quite sensitive, can be used to spot any developing trend toward loss of detector resolution. An abnormally high leakage current degrades the preamplifier's ability to differentiate the exact changes caused by gamma-rays impinging on the crystal. This, in turn, causes loss of resolution.

Most high-resolution germanium detector preamplifiers contain a test point to which a probe from a digital voltmeter can be attached. The initial measured voltage should be taken with a small amount of bias (~500 V) on the crystal. This value should be negative in the -0.1- to -1.5-V range. As bias is increased toward the operating bias, the measured voltage should spike sharply negative and then recover to a reading close to the initial value. Subsequent increases up to the detector operating voltage will yield a similar result, with the final measured voltage slightly more negative than the initial reading. The leakage current is then determined by the difference in the initial and final measured voltages divided by the value of the feedback resistor.

As an example, assume that the measured voltage at the 500-V bias is -0.23 V and that the measured voltage at the operating bias is -0.43 V; then, $\Delta V = 0.20$ V. Then, from $E = iR$, the leakage current for a feedback resistor value of 5×10^9 ohms would be

$$\frac{0.20\ \text{V}}{5 \times 20^9}\ \text{ohms} = 40\ \text{pA}.$$

The specification sheet accompanying a new germanium detector should state a maximum value for the leakage current. The manufacturer can supply the nominal value along with the value of the feedback resistor. When a new detector is received, the results of this test should be checked and recorded when making other pre-setup tests. As values are obtained periodically, they can be compared with the initial value, and possible trends toward detector deterioration might be observed on a more timely basis.

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APPENDIX B

PROCEDURES FOR QUALITY CONTROL OF GERMANIUM DETECTOR SYSTEMS

These procedures are generally acceptable for achieving quality control of germanium-based gamma-ray spectroscopy systems. Equivalent procedures may be used to achieve the same control of a system; in other words, these procedures point out the areas of concern and an approach to monitoring them.

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B.1 ENERGY CALIBRATION AND COUNT REPRODUCIBILITY CHECK

B.1.1 Purpose

To provide instructions for determining the energy calibration and checking the count reproducibility of germanium spectroscopy systems. Frequent determinations of the energy calibration allow a check of the electronic stability of the system with time. Also, a precise energy calibration is necessary for qualitative identification of gamma rays in a sample spectrum. Count rate reproducibility check is valuable in monitoring the stability of the counting efficiency of a detector with time.

B.1.2 Scope

These instructions are applicable to all gamma spectroscopy systems using germanium detectors.

B.1.3 References

None.

B.1.4 Abbreviations and Definitions*

germanium spectroscopy system: A gamma-ray spectroscopy system composed of an HPGe or a Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

slope: The slope of the line generated by plotting energy vs. channel number.

offset: The intercept on the energy axis of the line generated by plotting energy vs. channel number.

energy calibration: The process of determining the linear relationship between energy and channel number.

count reproducibility: The ability of a germanium spectroscopy system under fixed conditions of source-to-detector geometry and fixed counting time to reproduce a given number of counts from a known radioactive source within the limitations of Gaussian statistics.

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*All definitions are operational definitions and are not necessarily generally applicable.

B.1.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analyst and reviewing the entries in the logbooks periodically.

2. The analyst is responsible for calibrating all germanium spectroscopy systems each working day by following this procedure. The results of this check must be recorded in the appropriate logbook, and any abnormal results must be reported to the supervisor of the counting room. These data should be periodically reviewed for trends.

B.1.6 Procedure

B.1.6.1 Apparatus

Check source containing ^{109}Cd and ^{60}Co mounted on a source holder.

B.1.6.2 Instructions

1. Establish the settings of the instrument and experiment parameters required for normal operation of the spectroscopy system as listed in the logbook of the system.

2. Position the source and source holder on the endcap of the germanium detector.

3. Accumulate a spectrum for the time specified in the logbook and perform an energy calibration using the energy calibrate feature of the MCA, or calculate the slope and offset by using the equations in Section B.1.6.3 of this procedure.

4. If the slope is within the range of 0.999 to 1.001 for a 2048-channel spectrum or 0.499 to 0.501 for a 4096-channel spectrum and if the offset is within the range -2 to +2, omit instructions 5 through 7, and continue with instructions 8 and 9. If the slope or offset is not within the appropriate ranges specified above, proceed to step 5.

5. Using the zero adjustment of the system's ADC, set the peak channel of the 88.036-keV gamma ray of ^{109}Cd to channel 88 for a 2048-channel spectrum or channel 176 for a 4096-channel spectrum. This can be accomplished by visually inspecting the peak after accumulating a spectrum for a short period of time.

6. Adjust the fine gain on the amplifier so that the peak channel of the 1332.483-keV gamma ray of ^{60}Co is in channel 1332.5 for a 2048-channel spectrum or in channel 2665 for a 4096-channel spectrum.

7. Repeat instructions 5 and 6 until the peaks of the gamma lines are positioned to within ±1 channel of the desired positions, and then repeat instructions 3 and 4.

8. Determine the areas under the 88.0-keV and 1332.5-keV peaks by using a peak-search routine or manual calculation.

9. Record the fine gain, zero-level setting, the slope and offset of the energy calibration, and the areas under the 88.0-keV and 1332.5-keV peaks in the logbook. Plot the areas under the 88.0-keV and 1332.5-keV peaks on the appropriate control chart. Date and initial the entries, and report any abnormal settings or areas to the supervisor of the counting room.

B.1.6.3 Calculations for Energy Calibration

The slope m and offset a of the energy calibration can be calculated by

$$m = \frac{1332.483 - 88.036}{C_{1332} - C_{88}} \frac{\text{keV}}{\text{Ch}} = \frac{1244.457}{C_{1332} - C_{88}} \frac{\text{keV}}{\text{Ch}} , \qquad \text{(B.1)}$$

and

$$a = 88.036 \text{ keV} - mC_{88} , \qquad \text{(B.2)}$$

where

C_{88} = centroid or channel with the highest number of counts of the 88.036-keV, full-energy peak for ^{109}Cd,
C_{1332} = centroid or channel with the highest number of counts of the 1332.483-keV, full-energy peak for ^{60}Co.

B.2 BACKGROUND CHECK FOR GERMANIUM DETECTOR SYSTEM

B.2.1 Purpose

To provide instructions for determining the background of a germanium detector system. This procedure is necessary to monitor the fluctuations of background (e.g., noise) that directly affect the sensitivity of analyses obtainable with a germanium detector system.

B.2.2 Scope

These instructions are applicable to all germanium detector systems.

B.2.3 References

None.

B.2.4 Abbreviations and Definitions*

background: Any pulses stored by the germanium spectroscopy system in the absence of a radioactive sample.

germanium detector system: A system composed of an HPGe or Ge(Li) detector and a lead or steel shield.

germanium spectroscopy system: A system used for gamma-ray spectroscopy composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

B.2.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that the above procedure is followed by the analyst and reviewing the entries in the logbook periodically.
2. Each week an 8-h (28,800-s) background count should be run on all germanium detectors. The results of these checks should be recorded in an appropriate logbook, and any abnormal results should be reported to the supervisor of the counting room. These results should be reviewed periodically for trends.

B.2.6 Procedure

B.2.6.1 Apparatus

Germanium spectroscopy system.

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*All definitions are operational definitions and are not necessarily generally applicable.

B.2.6.2 Instructions

1. Establish the settings of the instrument and experiment parameters used during normal operation of the spectroscopy system as listed in the logbook of the system.

2. Remove all sources and blanks from the shield around the detector and close the shield.

3. Accumulate an 8-h (28,800-s) background spectrum. Save the spectrum on a system medium (disc or tape), or print out a hard copy of the spectrum.

4. Determine the nuclides present in the spectrum, report any background activities in the logbook, report any abnormal background activities to the appropriate supervisory personnel, and file a copy of those nuclides found in the spectrum in the appropriate file. (For computer-based systems, this would entail use of the nuclide report option for the system.)

5. Determine the total counts in the background for channels corresponding to the energy ranges of 50 to 1750 keV, 50 to 150 keV, 360 to 459 keV, 700 to 799 keV, and 1300 to 1399 keV. (These regions were chosen to obtain an estimate of the total background and the background in regions where gamma rays from naturally occurring radionuclides are not found.)

6. Record the sums of the counts in the specified energy ranges in the logbook, plot selected regions on control charts, date and initial the entries, and report any abnormal results to the supervisor of the counting room.

B.3 CHECK FOR FULL-ENERGY PEAK RESOLUTION AND PEAK-TO-COMPTON RATIO

B.3.1 Purpose

To provide instructions for determining the FEP resolution and peak-to-Compton ratio of a germanium detector. This procedure is necessary to ensure that the ability of a detector to discriminate photopeaks has not degraded with time.

B.3.2 Scope

These instructions are applicable to all gamma spectroscopy systems using germanium detectors.

B.3.3 Reference

1. Institute of Electrical and Electronics Engineers, Inc., Test Procedures for Germanium Gamma-Ray Detectors. IEEE Std. 325-1971. (ANSI N42.8 - 1972).

B.3.4 Abbreviations and Definitions*

full-energy peak (FEP): The peak in a spectrum due to complete interaction of a photon within the detector and complete collection of energy from this interaction.

resolution: Energy resolution in this context is a measure of the ability of a detector to separate closely spaced peaks.

full width at half maximum (FWHM): The full width of the peak at half the maximum magnitude of the peak.

peak-to-Compton ratio: The ratio of the maximum number of counts in the peak to the average of the flat portion of the Compton continuum. The flat portion of the Compton continuum is the 1040- to 1096-keV region for the 1332.52-keV gamma ray of ^{60}Co.

germanium spectroscopy system: A system used for gamma-ray spectroscopy composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

B.3.5. Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analyst and reviewing the entries in the logbooks periodically.

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*All definitions are operational definitions and are not necessarily generally applicable.

2. During the last week of each month the analyst shall determine the FEP resolution and the peak-to-Compton ratio for all germanium detectors. The results of these checks must be entered in the appropriate logbook, and any abnormal results should be reported to the supervisor of the counting room.

B.3.6. Procedure

B.3.6.1 Apparatus

1. Germanium spectroscopy system.
2. ^{57}Co and ^{60}Co point sources.

B.3.6.2 Instructions

1. Establish the settings of the instrument of the germanium spectroscopy system for the resolution check at 122.1 keV. (This might entail setting up the system for collection of a 4096-channel spectrum, calibrated so that each channel corresponds to about 0.2 keV.)
2. Center a ^{57}Co source on the endcap of the detector, and establish count rate for the full spectrum of 500 to 1500 counts per second by adjusting the vertical source-to-detector distance.
3. Acquire a spectrum with about 3000 counts in the peak channel for the gamma ray at 122.1 keV.
4. Perform an energy calibration using the 122.060- and 136.47-keV gamma rays.
5. Determine the FWHM of the 122.1-keV peak. This is accomplished by locating the centroid of the 122.1-keV peak and determining its magnitude, N_x (in counts). The magnitude of other channels in the 122-keV peak is determined until one channel on each side of the peak centroid is found that has one-half the magnitude (in counts) of the centroid channel. (Some interpolation of channel values is generally necessary to define the FWHM of the peak.) The difference in energy (keV) between the two channels defining the FWHM is considered to be the resolution of the detector. Simple calculator or computer programs may be developed to facilitate calculations of the FWHM for computer-based spectrometry systems. (For quality control procedures, the background need not be subtracted, because the procedure is used to detect changes in resolution.)
6. Establish the settings of the instrument of the germanium spectroscopy system for the check of resolution at 1332.5 keV and peak-to-Compton ratio. (Typically, this might entail setting up the system for collection of a 4096-channel spectrum, calibrated so that each channel corresponds to about 0.3 keV.)

7. Center the ^{60}Co source on the endcap of the detector, and establish a counting rate for the full spectrum of 500 to 1500 counts per second by adjusting the vertical source-to-detector position.

8 Accumulate a spectrum with more than 2000 counts in the peak channel of the 1332-keV line.

9. Perform an energy calibration using the 1173.226- and 1332.483-keV gamma lines of ^{60}Co.

10. Calculate the FWHM of the 1332.5-keV peak by the same method described in step 5.

11. Sum the counts found in the region 1040 to 1096 keV. Divide by the number of channels to obtain an average count per channel.

12. Calculate the peak-to-Compton ratio by dividing the peak channel counts in the 1332.5-keV peak by the average count per channel found in step 11.

13. Compare the calculated peak-to-Compton ratio with the original detector specification or the value last determined to see whether change has occurred.

B.4 CALIBRATION OF EFFICIENCY

B.4.1 Purpose

To provide instructions for determining the counting efficiency in various counting geometries used with germanium spectroscopy systems.

B.4.2 Scope

These instructions are applicable to all gamma spectroscopy systems using germanium detectors.

B.4.3 References

1. American National Standards Institute, Inc., Calibration and Usage of Germanium Detectors for Measurement of Gamma-Ray Emission Rates of Radionuclides. ANSI Guide N717 Draft 3, Revision 4, May 1977.

2. Coursey, B. M. Use of NBS Mixed Radionuclide Gamma-Ray Standards for Calibration of Ge(Li) Detectors Used in the Assay of Environmental Radioactivity. In: Measurements for the Safe Use of Radiation. National Bureau of Standards, Gaithersburg, Maryland, 1976. pp. 173-179.

B.4.4 Abbreviations and Definitions*

germanium spectroscopy system: A system used for gamma-ray spectroscopy composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

full-energy peak (FEP): The peak in a spectrum due to complete interaction of a photon within the detector and complete collection of energy from this interaction.

counting efficiency: That part or fraction of the total number of gamma rays emitted by a radioactive source that is detected and registered in the FEP by the germanium spectroscopy system with a given counting geometry. May be expressed as a fraction or percentage.

counting geometry: The conditions of space and volume in which a sample is counted using a germanium spectroscopy system.

B.4.5 Responsibilities

1. The counting efficiency for all systems for all counting geometries used by the laboratory for gamma-ray spectroscopy using germanium

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*All definitions are operational definitions and are not necessarily generally applicable.

detectors should be determined yearly, when changes occur in count rate reproducibility (see Section B.1), or when a new germanium detector is received. After completion of calibration, pertinent information (Section B.4.6.2.10) should be recorded in an appropriate logbook and approved by the supervisor of the counting room.

B.4.6 Procedure

B.4.6.1 Apparatus

1. Sources containing a mixture of radionuclides prepared in the various counting geometries. When counted, the counting rate for the total spectrum of these standards should be less than 1000 counts per second.
2. Germanium spectroscopy system.

B.4.6.2 Instructions

1. Establish the settings of the instruments as used for routine operation of the germanium spectroscopy system.
2. Position the source on the detector endcap, and accumulate a spectrum with at least 20,000 counts in all peaks to be used in determining efficiency.
3. Determine the net areas of peaks to be used in the calibration of efficiency. (This may be accomplished by a computer "peak search" routine or by manual calculations.)
4. Areas of potential problems

   a. If ^{60}Co and ^{88}Y are present, care should be taken when determining the count rate of the 1332.5-keV peak of ^{60}Co because the single escape peak (1324.1 keV) from the 1836.1-keV gamma ray ^{88}Y may interfere.

   b. If ^{85}Sr is present, caution should be exercised when determining the count rate of the 514.0-keV peak because of its close proximity to the 511.0-keV annihilation peak.

   c. If ^{109}Cd is present, care should be taken when determining the count rate of the 88.0-keV peak because of the high background in this region resulting from the Compton continuum. X rays from ^{203}Hg or other nuclides with a high atomic number may also interfere with the 88.0-keV peak.

   d. In general, peaks in high continuum regions, in the X-ray region (less than 100 keV), and in close proximity to background or escape peaks should be carefully analyzed.

5. Calculate the efficiencies using appropriately determined values of counts per second for each FEP. Counting efficiency is calculated from a ratio of the observed counting rate to the value of disintegrations per second supplied with the source material for each gamma-ray energy. (The observed counting rate must be corrected for gamma-ray branching ratios. Similarly, the expected count rate for each nuclide must be corrected to the time of counting.)

6. Compare calculated efficiencies with a model and with values of efficiency determined in previous years. A log-log, least-squares regression may be performed on the new data to model the relationship of energy to efficiency (for energies greater than 270 keV.)

7. Compare efficiencies determined by the least-squares regression with values determined in previous years. Unless prior efficiencies are known to be in error, average the new and old values. Report the calculated values to the supervisor of the counting room.

8. With the approval of the counting room supervisor, prepare new tables and graphs on counting efficiency. For computer-based germanium spectroscopy systems, enter the new efficiencies into the appropriate efficiency file of the computer.

9. Prepare several copies of the table and file on efficiency.

10. One copy of the table and file is added to the logbook of the appropriate germanium detector, along with the appropriate information necessary to recreate the calculated efficiencies at a later time: (a) the NBS standard identification number, (b) all dilution factors, (c) the code number of the quality control (QC) logbook for the sample and the page number in the QC logbook where the preparation of the standard is recorded, (d) a copy of the original certification for the standard, (e) branching fractions used to convert from disintegrations per second to gammas per second, (f) a list of all counting rates determined for each point on the efficiency curve, and (g) a description of the counting geometry used. This information should be put into tabular form (as possible) to save space in the logbook.

B.5 CHECK ON SYSTEM LINEARITY

B.5.1 Purpose

To provide instructions for checking the linearity of the ADC, preamplifier, and amplifier of a germanium spectroscopy system. This procedure is necessary because precise and linear amplification and sorting of pulses are essential for accurate gamma-ray spectroscopy.

B.5.2 Scope

These instructions are applicable to all gamma spectroscopy systems that use germanium detectors.

B.5.3 References

None.

B.5.4 Abbreviations and Definitions*

ADC: Analog-to-digital converter.

germanium spectroscopy system: A system for gamma-ray spectroscopy composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

linearity (integral linearity): The linear relationship between the amplitude of the pulse, which is proportional to energy, and the channel in which the pulse is stored.

B.5.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analyst and reviewing the entries in the logbooks periodically.
2. At the beginning of each quarter, after major repair of an instrument, or when a new ADC, amplifier, or detector is received, the analyst shall check linearity of all germanium detector systems. The results of this check must be entered in the appropriate logbook, and abnormal results must be reported to the supervisor of the counting room. These data should be reviewed periodically.

B.5.6 Procedure

B.5.6.1 Apparatus

1. Germanium spectroscopy system.
2. Point source containing a mixture of radionuclides such as that prepared by NBS. The NBS source contains ^{109}Cd, ^{203}Hg, ^{85}Sr, ^{57}Co, ^{60}Co, ^{88}Y, ^{137}Cs, ^{113}Sn, ^{139}Ce and has gamma-ray lines at 88.036, 122.060, 165.854, 391.689, 513.998, 661.630, 898.00, 1173.226, 1332.483, and 1836.075 keV.
3. Holder for the source with a 4-cm spacing.

B.5.6.2 Instructions

1. Establish the instrument settings (listed in the logbook for the system) to be used for the check of system linearity.

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*All definitions are operational definitions and are not necessarily generally applicable.

2. Position the holder for the source and the point source on the detector endcap.

3. Accumulate a spectrum for the time specified in the logbook.

4. Perform an energy calibration on the spectrum using the 88.036-keV line of ^{109}Cd and 1332.483-keV line of ^{60}Co as the calibration points.

5. Determine the channel location and corresponding energies for the 122.060-, 165.854-, 391.689-, 661.630-, 898.00-, 1173.226-, and 1836.075-keV peaks. (This may be done by manual calculation or by use of peak search routines.) Calculate the difference between the determined energies for these peaks and the actual energy. Record the results in the appropriate logbook, and report any differences greater than ±0.8 keV to the supervisor of the counting room.

B.6 CHECK OF THE MCA ELAPSED-TIME CLOCK

B.6.1 Purpose

To provide instructions for checking the elapsed-time clock of the MCA. This procedure is necessary to ensure that accurate measurements of counting time can be achieved.

B.6.2 Scope

These instructions are applicable to all ADC-MCA systems equipped with live-time clocks.

B.6.3 References

None.

B.6.4 Abbreviations and Definitions*

ADC: Analog-to-digital converter.

MCA: Multichannel analyzer.

ADC-MCA system: ADC and MCA that are used in combination.

elapsed time: The actual "clock time" between the start of data acquisition and the termination of data acquisition.

B.6.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analytical chemist.
2. The analytical chemist is responsible for performing this procedure on all ADC-MCA systems at the beginning of each year, after major repair to the ADC or MCA, when a new ADC or MCA is received, or when the ADC-MCA configuration is changed. The results of these checks must be entered in the appropriate logbook, and any abnormal results must be reported to the supervisor of the counting room.

B.6.6 Procedure

B.6.6.1 Apparatus

1. ADC-MCA system.
2. Amplifier.

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*All definitions are operational definitions and are not necessarily generally applicable.

3. Pulser with precision repetition rate.
4. Calibrated oscilloscope.

B.6.6.2 Instructions

1. Disconnect all inputs to the amplifier.

2. Establish settings of the instrument as listed in the logbook for the check of MCA elapsed-time clock.

3. Connect the output of the pulser to the input of the amplifier, and collect a spectrum for the time specified in the logbook.

4. Sum the counts stored in the MCA, record the sum in the logbook, and date and initial the results. If the sum deviates from the expected value by more than 0.3 percent, report the deviation to the supervisor of the counting room.

B.7 MCA LIVE-TIME CLOCK CHECK

B.7.1 Purpose

To provide instructions for checking the accuracy of the system live-time clock of the ADC-MCA system. Accurate compensation for "dead time" in the MCA due to pulse pile-up at high count rates is essential to ensure that the analyzer will accept signal pulses from a source for the same total time, regardless of count rate.

B.7.2 Scope

This procedure is applicable to all gamma spectroscopy systems that use an MCA.

B.7.3 Reference

1. Crouch, D. F., and R. L. Heath. Routing Testing and Calibration Procedures for Multichannel Pulse Analyzers and Gamma Ray Spectrometers. IDO-16923, November 1963.

B.7.4 Abbreviations and Definitions*

ADC: Analog-to-digital converter.

MCA: Multichannel analyzer.

ADC-MCA system: ADC and MCA that are used in combination.

live time: That time during which the ADC-MCA combination is capable of accepting and recording a pulse.

live-time clock: A clock that records only the live time.

dead time: That time during which the ADC-MCA combination is not capable of accepting and recording a pulse.

B.7.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analytical chemist and reviewing the entries in the logbooks periodically.

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*All definitions are operational definitions and are not necessarily generally applicable.

2. The analytical chemist shall perform a check on the live-time clock on each ADC-MCA system annually, after major repair of an ADC or MCA, or when a new ADC or MCA is received. The results of these checks must be entered in the appropriate logbook, and abnormal results must be reported to the supervisor of the counting room.

B.7.6 Procedure

B.7.6.1 Apparatus

1. Germanium spectroscopy system.
2. One ^{109}Cd source (with an activity of about 150 μCi).
3. One pulser with a precision repetition rate.

B.7.6.2 Instructions

1. Establish the settings of the instrument to be used for the check on the MCA live-time clock as listed in the logbook. (This typically might involve a 2048-channel spectrum and a preset live time of 100 s.)

2. Connect the pulser to the input of the amplifier and establish a repetition rate of about 100 pulses per second in the region of channel 1700 for a 2048-channel spectrum.

3. Acquire two or more spectra for a live time of 100 s and sum the counts due to the pulser (C_{po}).

4. Place the ^{109}Cd source in the shield, and establish a counting rate for the full spectrum of 1900 to 2100 counts per second. (The ^{109}Cd source can be located at any position within the shield, and the count rate can be varied by changing the distance between the source and the detector.)

5. Acquire two or more spectra for live times of 100 s, and sum the counts due to the pulser (C_{ps}). (The region summed should be broader than in step 3 because of the effects of counting rate and summing.) Summing of pulses from ^{109}Cd and the pulser will cause certain pulses to be stored in regions above the main peak generated by the pulser, while the increase in counting rate will cause the pulser-generated peak to broaden.

6. Acquire a 100-s count with the source removed from the shield, and sum the counts due to the pulser. This will confirm that the repetition rate of the pulser has not changed.

7. Repeat steps 4 through 6, but establish a counting rate for the full spectrum of 4900 to 5100 counts per second.

8. Repeat steps 4 through 6, but establish a counting rate for the full spectrum of 9800 to 10,200 counts per second.

9. In the logbook, record the average values for C_{po}, C_{ps}, and the quantity 100% $(C_{ps} - C_{po})/C_{po}$ for the three counting rates. The latter quantity is the percentage gain or loss of the live times. Date and initial the results, and report the results to the supervisor of the counting room.

B.8 ADJUSTMENT OF THE POLE/ZERO CANCELLATION AND THE DC LEVEL

B.8.1 Purpose

To provide instructions for adjusting the pole/zero compensation and the DC level of an amplifier used with a germanium spectroscopy system. Proper adjustment of these settings of an amplifier is necessary to ensure proper processing of a signal pulse by an ADC-MCA system.

B.8.2 Scope

These instructions apply to all amplifiers used with germanium spectroscopy systems.

B.8.3 References

1. Princeton Gamma Tech, Inc. Princeton Gamma Tech Model 340 Spectroscopy Amplifier Operating Manual. February 1976.
2. Canberra Industries. Canberra Model 1413 Spectroscopy Amplifier Operating Manual.

B.8.4 Abbreviations and Definitions*

germanium spectroscopy system: A system used for gamma-ray spectroscopy composed of an HPGe or Ge(Li) detector, an amplifier, an ADC, an MCA, and a lead or steel shield.

pole/zero: A potentiometer used to compensate for the undershoot caused by the fall-time constant of the preamplifier.

DC level: The output of the DC output voltage of the unipolar output with no signal input to the amplifier.

B.8.5 Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analytical chemist and reviewing the entries in the logbook periodically.

2 At the beginning of each quarter, after a change in the time constant, after major repair of an instrument, or when a new detector or amplifier is received, the analytical chemist must check the pole-zero and DC-level adjustments of each amplifier used in a germanium spectroscopy system. The results of these checks must be recorded in the appropriate logbook, and abnormal results must be reported to the supervisor of the counting room immediately.

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*All definitions are operational definitions and are not necessarily generally applicable.

B.8.6 Procedure

B.8.6.1 Apparatus

1. Oscilloscope.
2. Jeweler's screwdriver.
3. Check source (^{137}Cs).
4. Coaxial cable with BNC connectors (5 to 10 m long).

B.8.6.2 Adjustment of the DC-Level

1. Establish the settings of the amplifier to levels normally used during routine operation of the spectroscopy system, as listed in the logbook of the system.

2. Remove all radioactive sources from the shield, and close the shield.

3. Set the oscilloscope for a deflection of 20 mV/cm and a sweep speed of 10 μs/cm, and connect the unipolar output of the amplifier to the input of the oscilloscope.

4. Adjust the DC level so that the trace on the oscilloscope does not shift appreciably when the signal cable to the oscilloscope is connected and disconnected.

B.8.6.3 Pole/Zero Adjustment

1. Establish the settings of the amplifier to levels normally used during routine operation of the spectroscopy system.

2 Place the ^{137}Cs source on the detector endcap, and establish a counting rate of about 300 counts per second in the FEP by proper spacing of the source above the detector.

3. Set the oscilloscope for a deflection of 100 mV/cm and a sweep speed of 10 μs/cm.

4. Connect the unipolar output of the amplifier to the input of the oscilloscope.

5. Adjust the pole/zero potentiometer of the amplifier to bring the noise to a flat baseline. (Consult page 20 of Reference 1, Section B.8.3.3, for a pictorial representation of a proper pole-zero setting.)

B.9 CHECK OF THE SYSTEM NOISE

B.9.1 Purpose

To provide instructions for determining the system noise of a germanium detector, preamplifier, and amplifier. Accurate documentation of noise of the system during normal operation is useful for comparative purposes if additional noise or malfunction in the system is suspected.

B.9.2 Scope

These instructions are applicable to all systems using a germanium detector.

B.9.3 References

None.

B.9.4 Abbreviations and Definitions*

germanium detector system: A system consisting of an HPGe or Ge(Li) detector, a preamplifier, and an amplifier.

noise: Any pulses other than those due to photon interaction of a photon in the detector.

B.9.5. Responsibilities

1. The supervisor of the counting room is responsible for ensuring that this procedure is followed by the analytical chemist and reviewing the entries in the logbook periodically.
2. The analytical chemist is responsible for performing a check of noise on all germanium spectroscopy systems at the beginning of each quarter, after major repair to the detector, amplifier, or preamplifier, or when a new detector or amplifier is received. The results of these checks must be entered in the appropriate logbook, and any abnormal results must be reported to the supervisor of the counting room immediately.

B.9.6 Procedure

B.9.6.1 Apparatus

1. Germanium detector system.
2. Oscilloscope.
3. Coaxial cable with BNC connections (5 to 10 m long).

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*All definitions are operational definitions and are not necessarily generally applicable.

B.9.6.2 Instructions

1. Remove all radioactive sources from the shield, and close the shield.

2. Establish the settings of the amplifier to those specified in the logbook.

3. Observe the unipolar output of the amplifier at the gain and oscilloscope settings listed in the logbook. Record the value of the observed peak-to-peak noise, and sketch or photograph any apparent waveforms if they exist. Date and initial the entries in the logbook. Report any abnormal results to the appropriate supervisory personnel.